

Controlled Release Environmental Reactants:

A More Efficient Approach to In
Situ Remediation

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Controlled Release Reactants

What are the Methods
and Materials?



3rd Party Validation

Independently researched and published by several universities including:

- Ohio State
- Purdue
- University of Nebraska
- Clemson
- Colorado School of Mines
- UNC A&T
- Clarkson University



3rd Party Validation

Currently the subject of DOD/DOE
field study: ESTCP Proj# ER-201324

- “Sustained In Situ Chemical
Oxidation (ISCO) of 1,4-Dioxane
Using Slow Release Chemical
Oxidant Cylinders”
- Demonstration Site: Naval Air
Station North Island (**San Diego**)



References:

Links to 3rd party publications can also be found on our website at:

www.sesciences.com/technical-library

Specialty Earth Sciences IP:

US Patent No: 7,431,849
US Patent No: 8,210,773
US Patent No: 8,366,350
US Patent No: 9,061,333
US Patent No: 9,611,421
Japanese Patent No: 6,058,708
US Pat App No: 12-269,520
US Pat App No: 14-024,046
US Pat App No: 14-920,370
US Pat App No: 15-450,369
US Pat App No: 15-342,845
US Pat App No: 15-014,308
US Pat App No: 15-198,702
EU Pat App No: 09 826 642.2-1371

- Yang 2016 – “To postpone the precipitation of manganese oxides in the degradation of tetrachloroethylene by controlling the permanganate concentration”
 - <http://dx.doi.org/10.1080/09593330.2016.1184320>
- Chainarong 2016 – “Oxidation of 17B-Estradiol in Water by Slow-Release Permanganate Candles”
 - <http://doi:10.1089/ees.2015.0456>
- Yao 2016 – “Radial basis function simulation of slow-release permanganate for groundwater remediation via oxidation”
 - <https://doi.org/10.1016/j.cam.2016.02.006>
- Chantat 2015 – “Treating Methyl Orange in a Two-Dimensional Flow Tank by In Situ Chemical Oxidation Using Slow-Release Persulfate Activated with Zero-Valent Iron”
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 - <http://dx.doi.org/10.1080/09593330902840342>
- Luster-Teasley 2009 – “Encapsulation of Potassium Permanganate Oxidant in Polymers”
 - http://books.google.com/books?id=RYE6YKPdFDEC&pg=PA278&ots=pd_BMxiUaZ&dq=Luster%20teasley%20proceedings%20of%202007&pg=PA278#v=onepage&q=Luster%20teasley%20proceedings%20of%202007&f=false
- Lee 2007 – “Efficacy of controlled-release KMnO₄ (CRP) for controlling dissolved TCE plume in groundwater: A large flow-tank study”
 - <http://dx.doi.org/10.1016/j.chemosphere.2008.10.062>
- Lee 2007 – “Characterization and optimization of long-term controlled release system for groundwater remediation: a generalized modeling approach”
 - <http://dx.doi.org/10.1016/j.chemosphere.2007.04.037>
- Lee 2007 – “Characteristics and applications of controlled-release permanganate for groundwater remediation”
 - <http://dx.doi.org/10.1016/j.chemosphere.2006.09.093>
- Ross 2005 – “Characteristics of Potassium Permanganate Encapsulated in Polymer”
 - [http://dx.doi.org/10.1061/\(ASCE\)0733-9372\(2005\)131:8\(1203\)](http://dx.doi.org/10.1061/(ASCE)0733-9372(2005)131:8(1203))



Key Concepts:

CONTROL IMPLEMENTATION COSTS:

- No expensive injection field services required
- Use your preferred driller
- Implementation can be achieved by on-site consultant

CONTROL REACTANT DISTRIBUTION:

- Apply reactants where they belong without guessing where chemical is going
- Apply reactants in sufficient mass required (Ex: 500 lbs oxidant in 10'x10" auger boring)

Technology

- **Safer and more effective** approach to ISCO
- Delivers high concentration reactants to the target and remains active for **longer periods** of time (several months to a couple of years – depending on material selection)
- Addresses the **common problems and technical challenges** encountered with traditional pressurized liquid injection applications:



1. **Relatively short period of oxidant activity in subsurface**
2. **Contaminant contact problems - injected oxidants take the path of least resistance (flow-by)**
3. **Problem geologies: low permeable media (LPM)**
4. **Site logistics – ISCO events are cumbersome and can be disruptive to active facilities**



Technology

- Involves coating or encapsulating granular environmental reactants for a **more efficient** and **user-friendly** implementation
- These materials can be applied to the subsurface in a **number of forms and methods.....**



MULTIPLE SHAPES

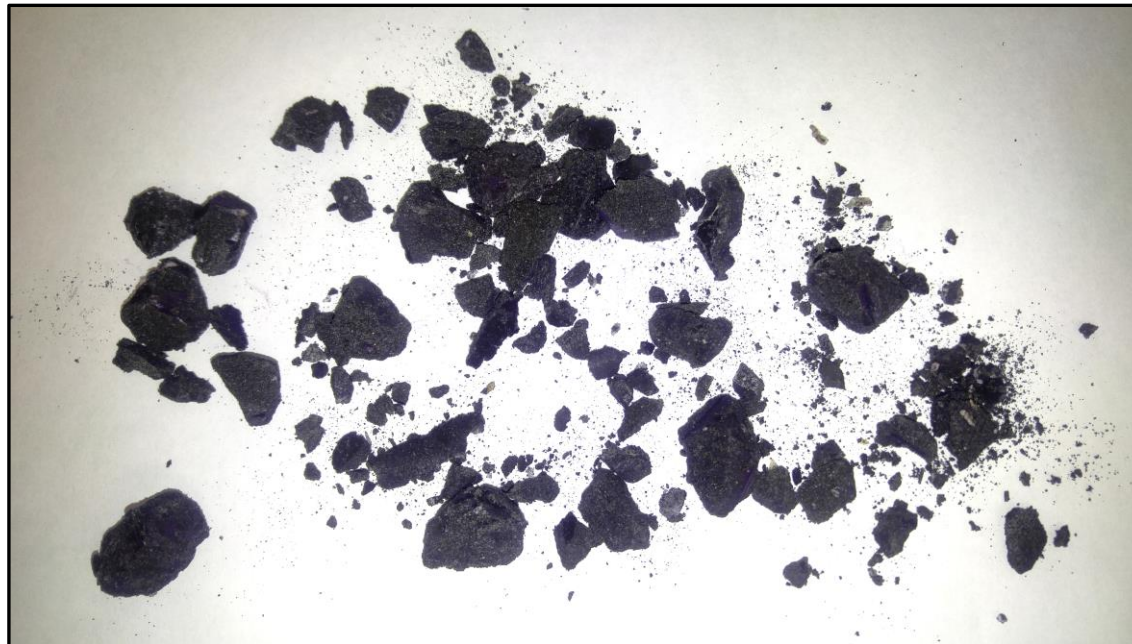
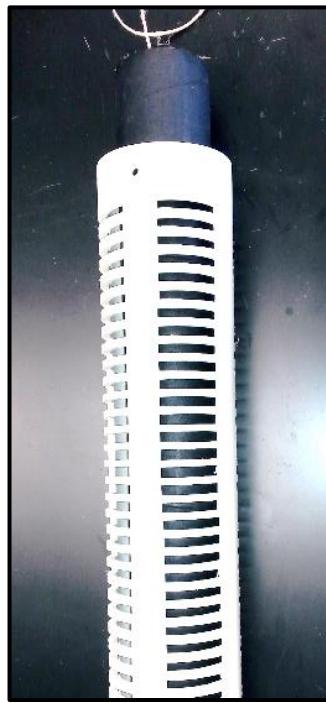
MULTIPLE SIZES

SEVERAL CHEMISTRIES



Material Forms

- Cylinders
- Spheres
- Granules
- Pellets



Installation Methods

Horizontal Wells



Direct Borehole Installation



Down-Well Installation



Excavation Closure



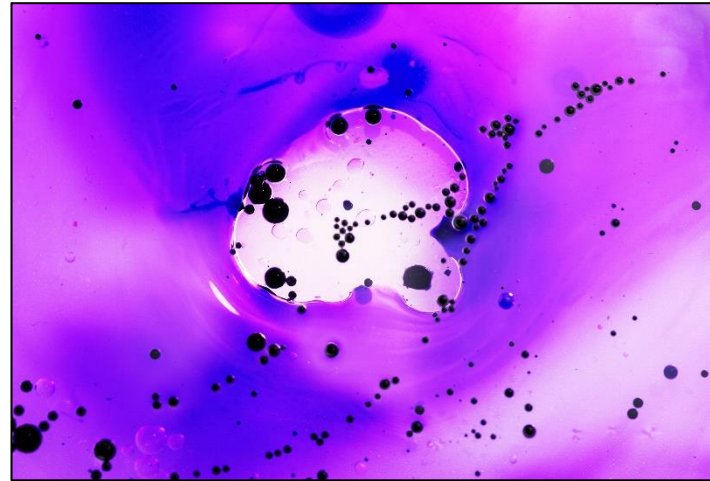
Mechanism Of Reactant Release

1) Sustained Reactant Release



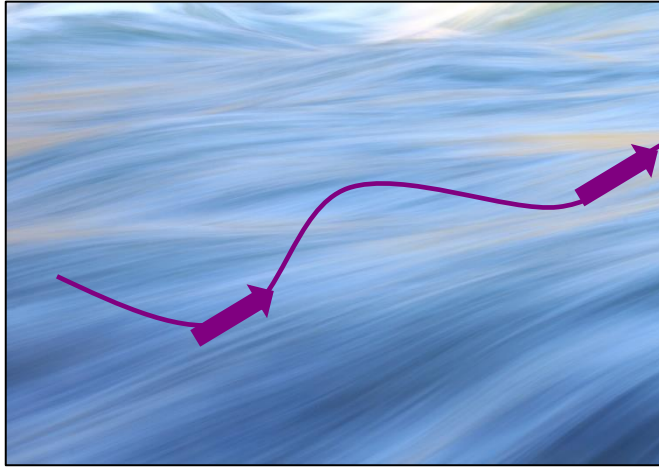
Slow/sustained reactant release over time is the prevailing MRR in dissolved phase contaminant conditions

2) Targeted Reactant Release

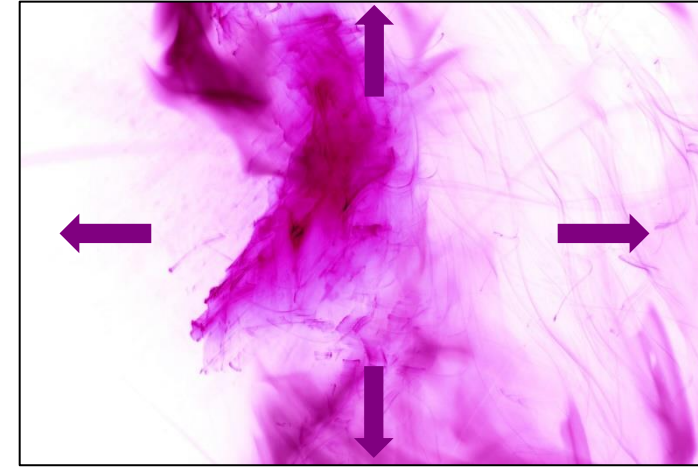


- In the presence of NAPL reactants will be preferentially released in high concentration
- Targeted release is governed by the effects of hydrocarbon partitioning

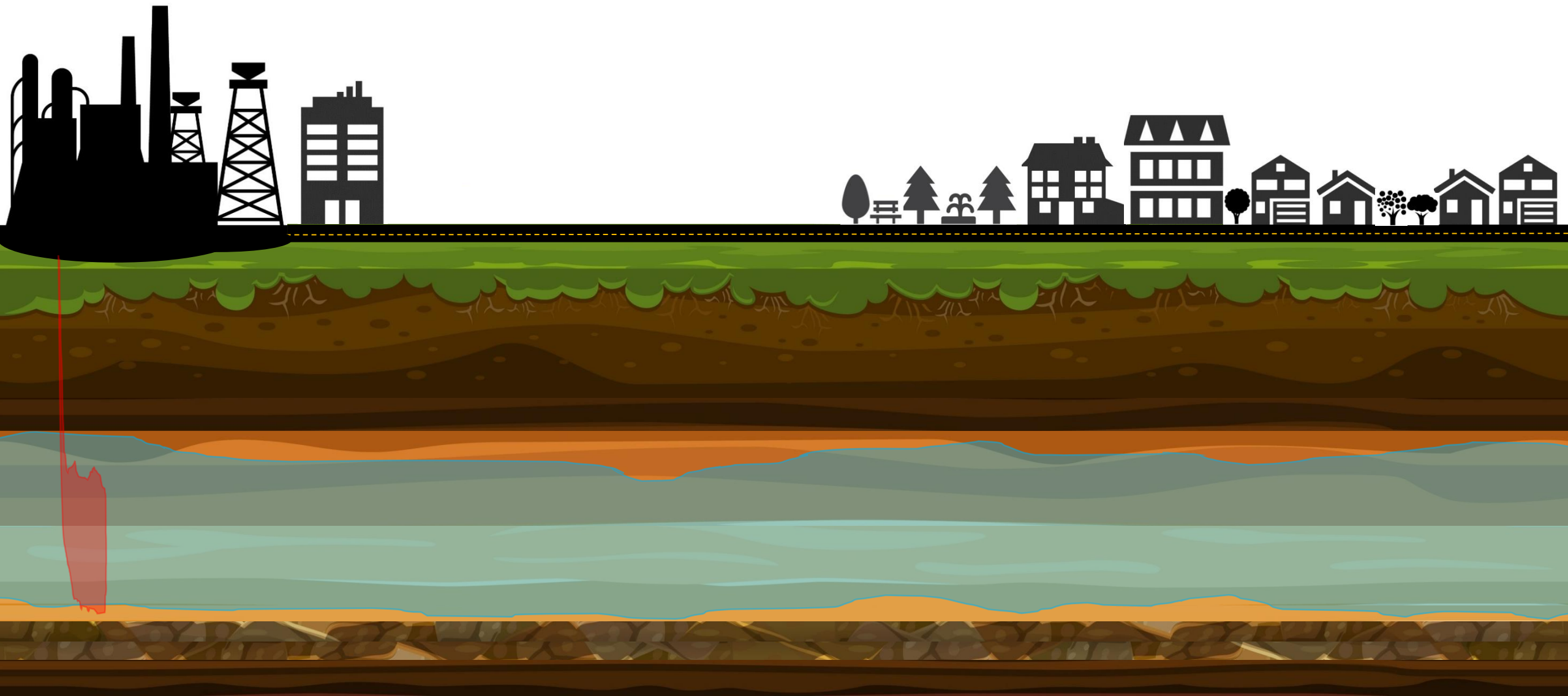
1. **Advective flow** governs reactant transport in **transmissive** formations



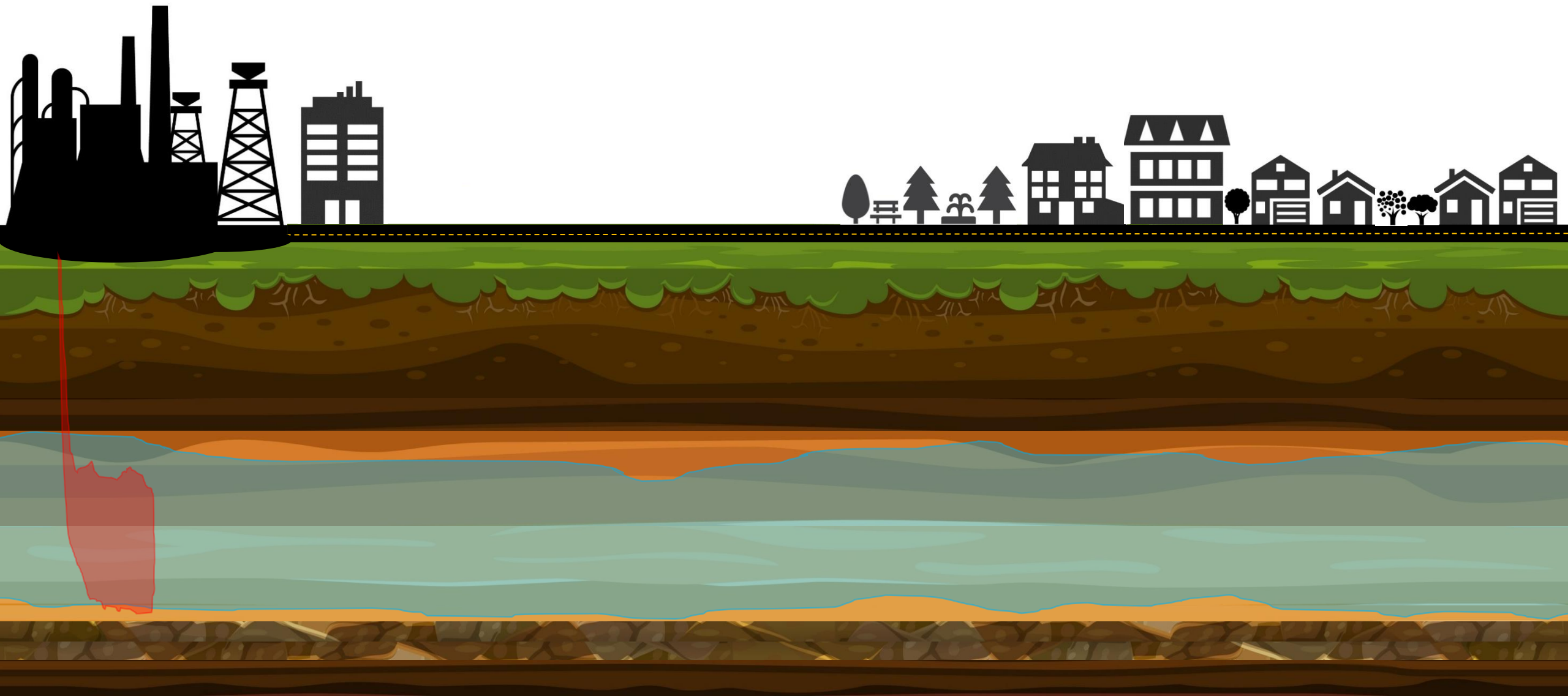
2. Concentration gradient driven **diffusion** governs transport in low permeability, **perched formations**



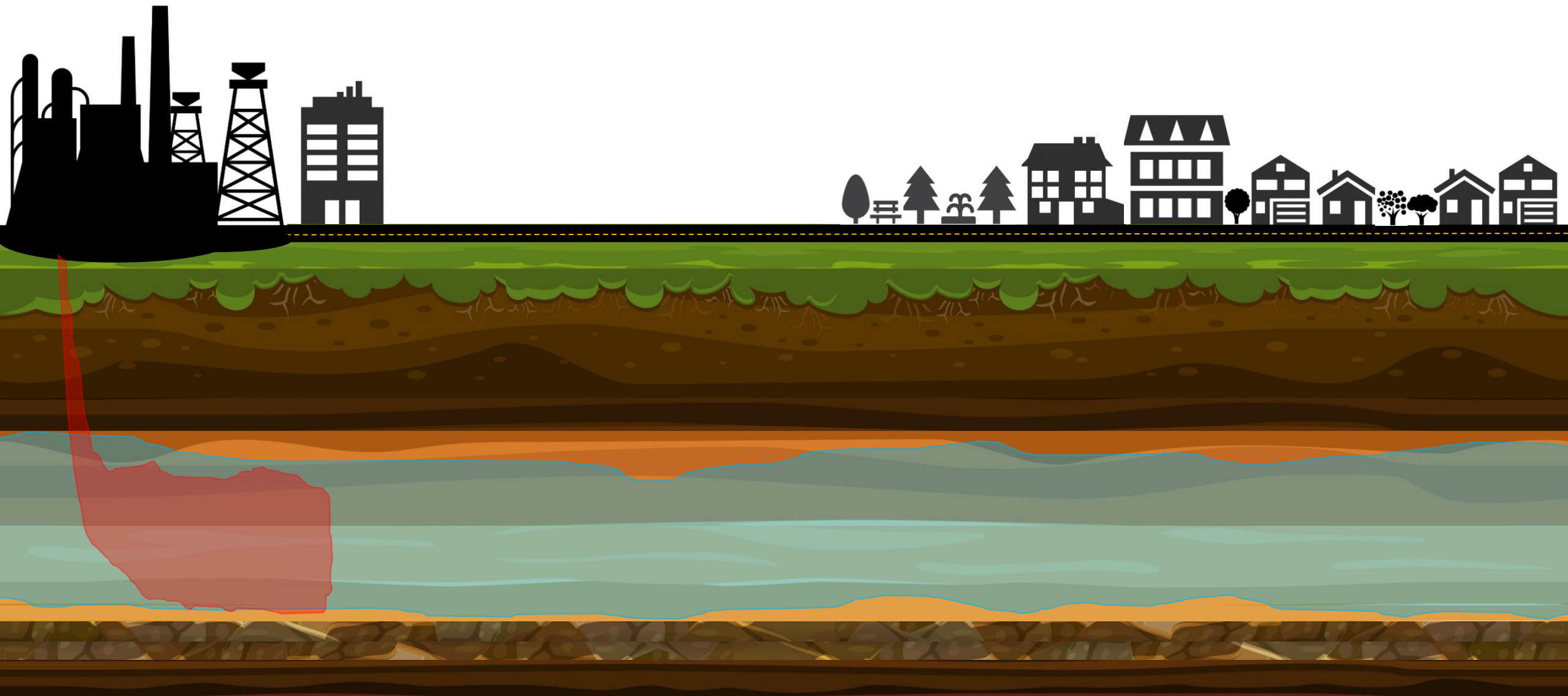
Transport Kinetics



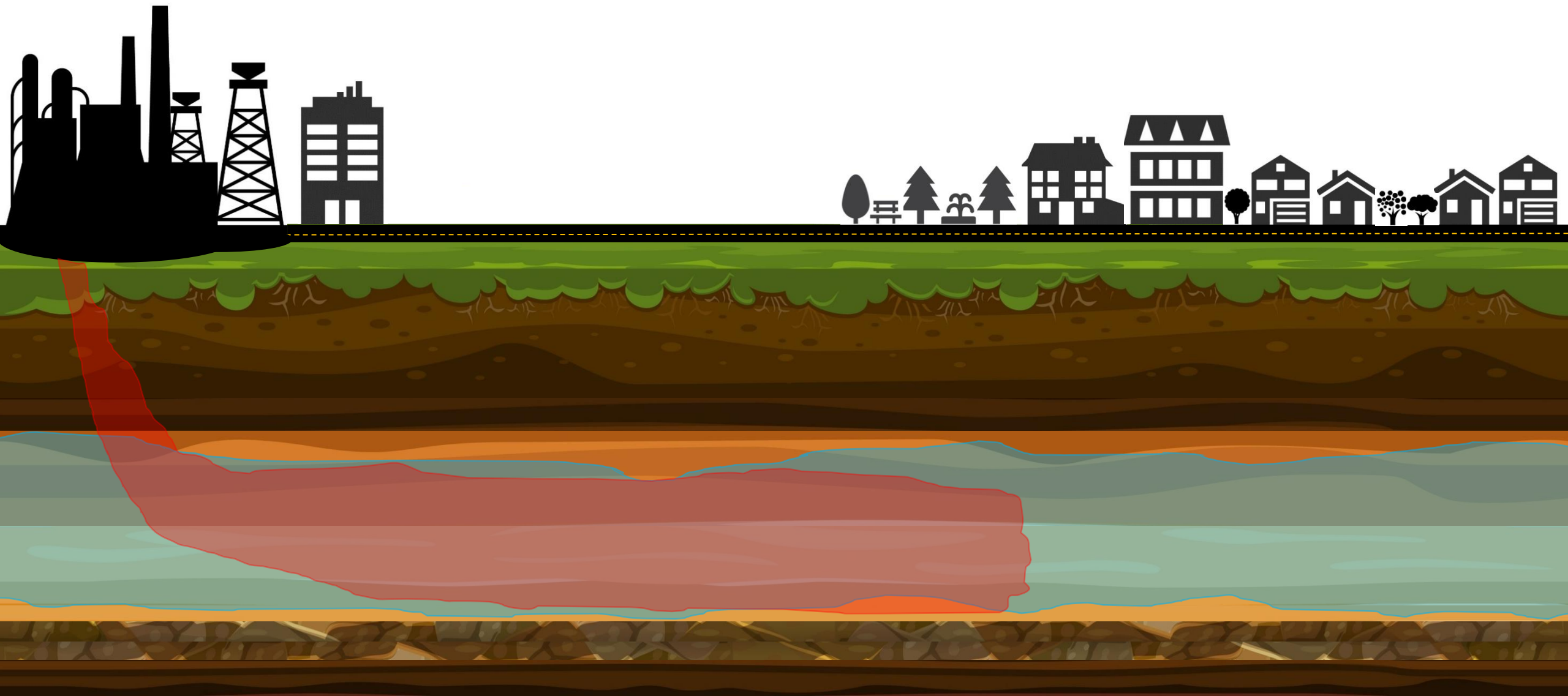
Groundwater contamination



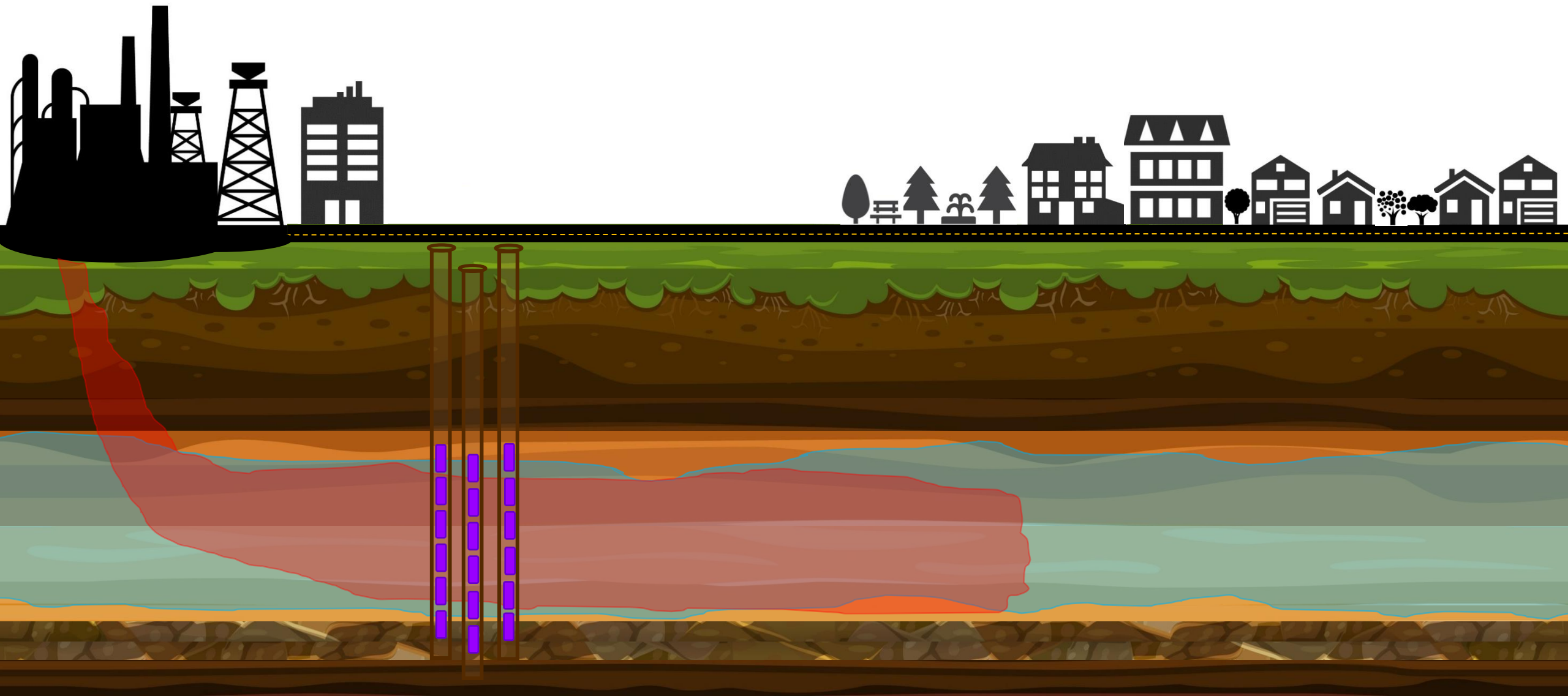
Plume migration



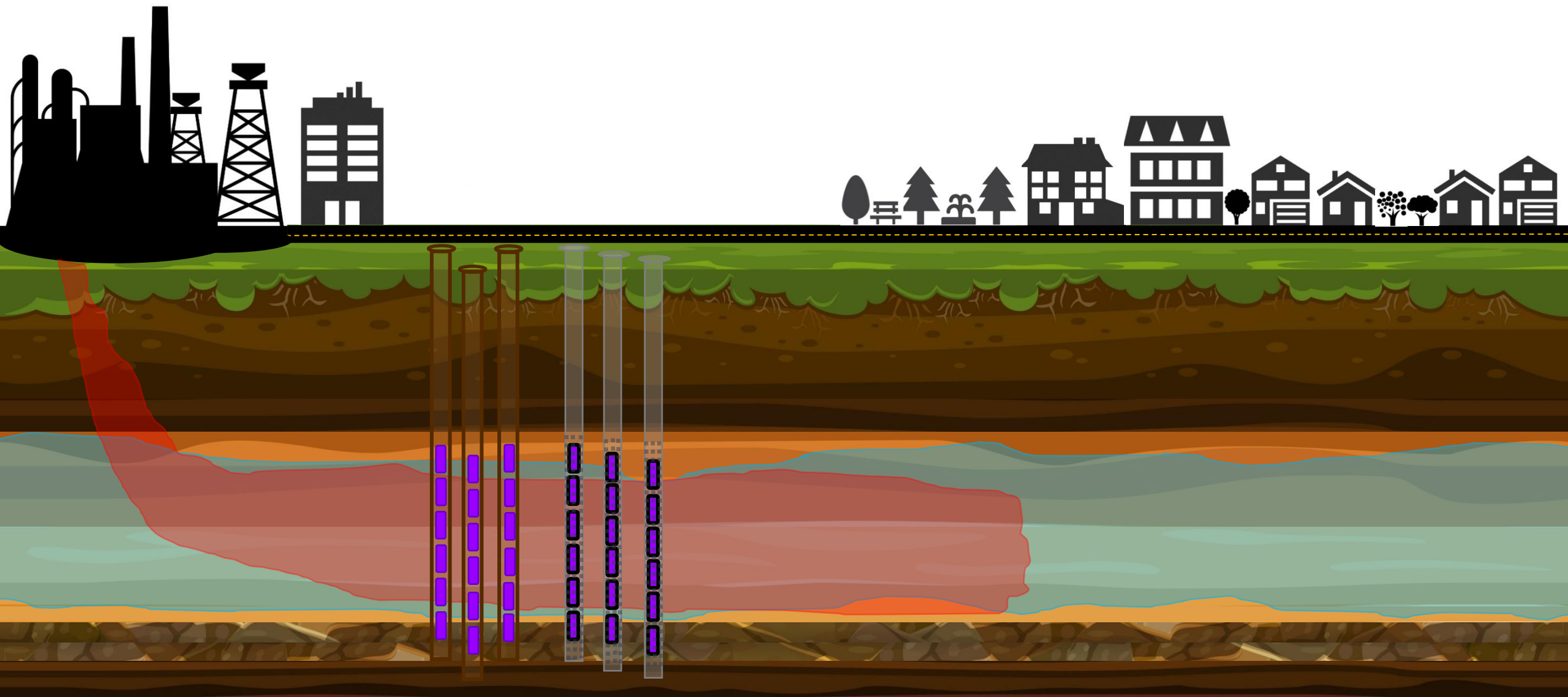
Further plume migration



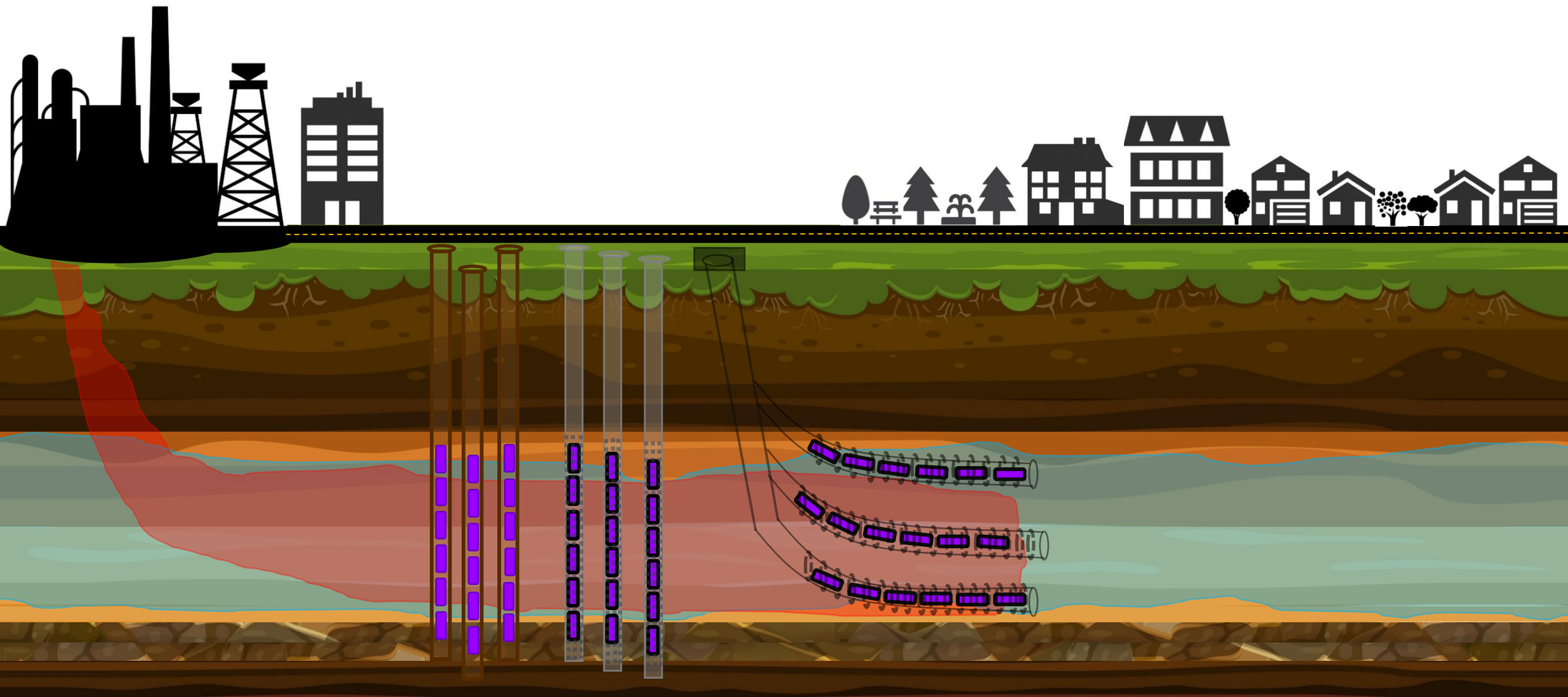
.....and further



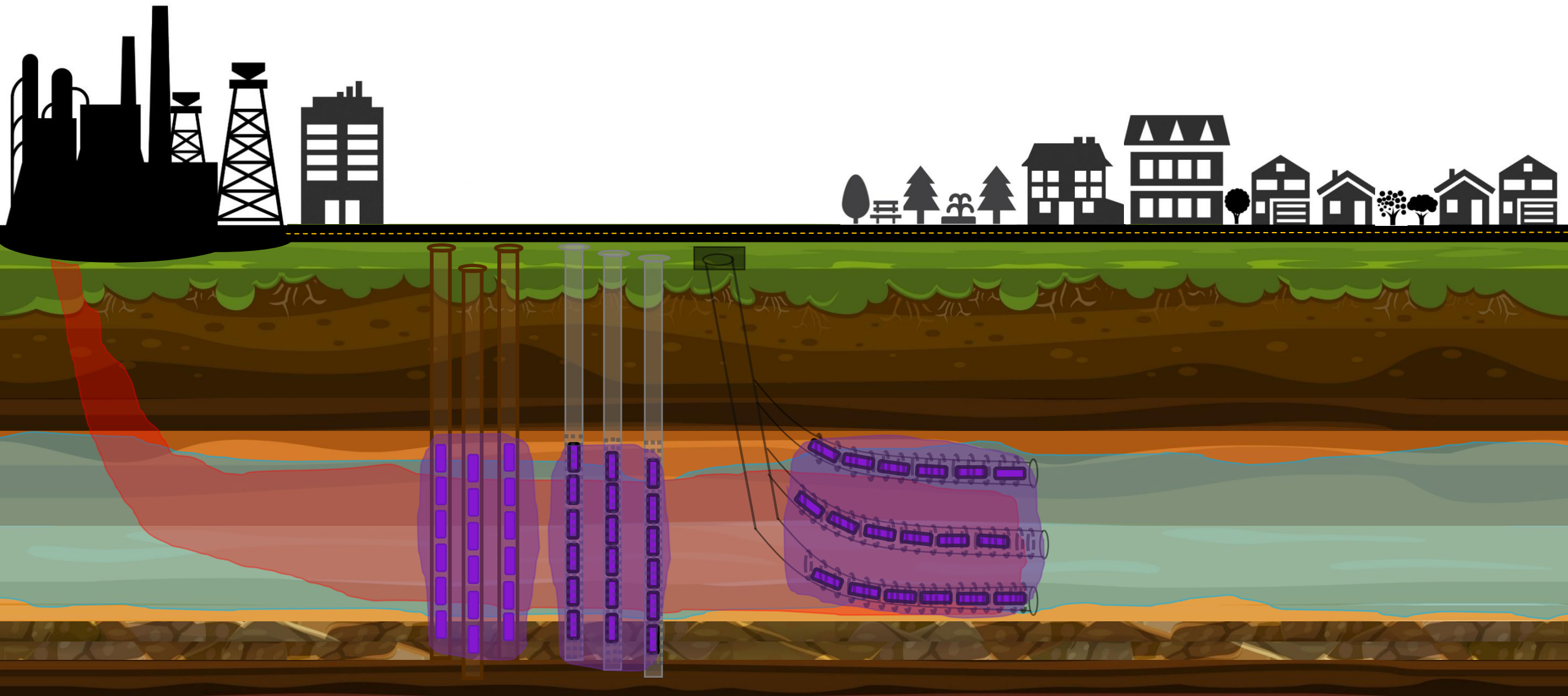
SOCORE – borehole/DPT/auger installation



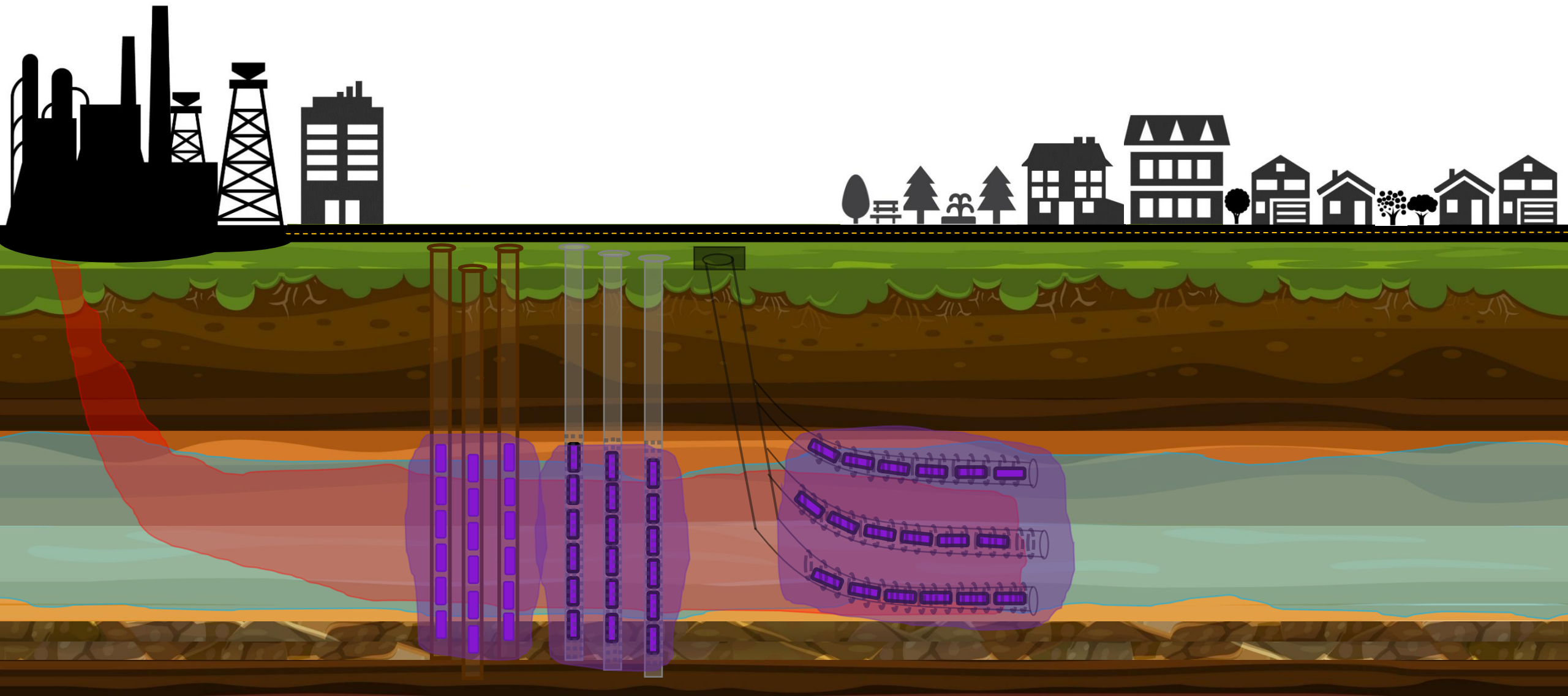
SOCORE – well installation



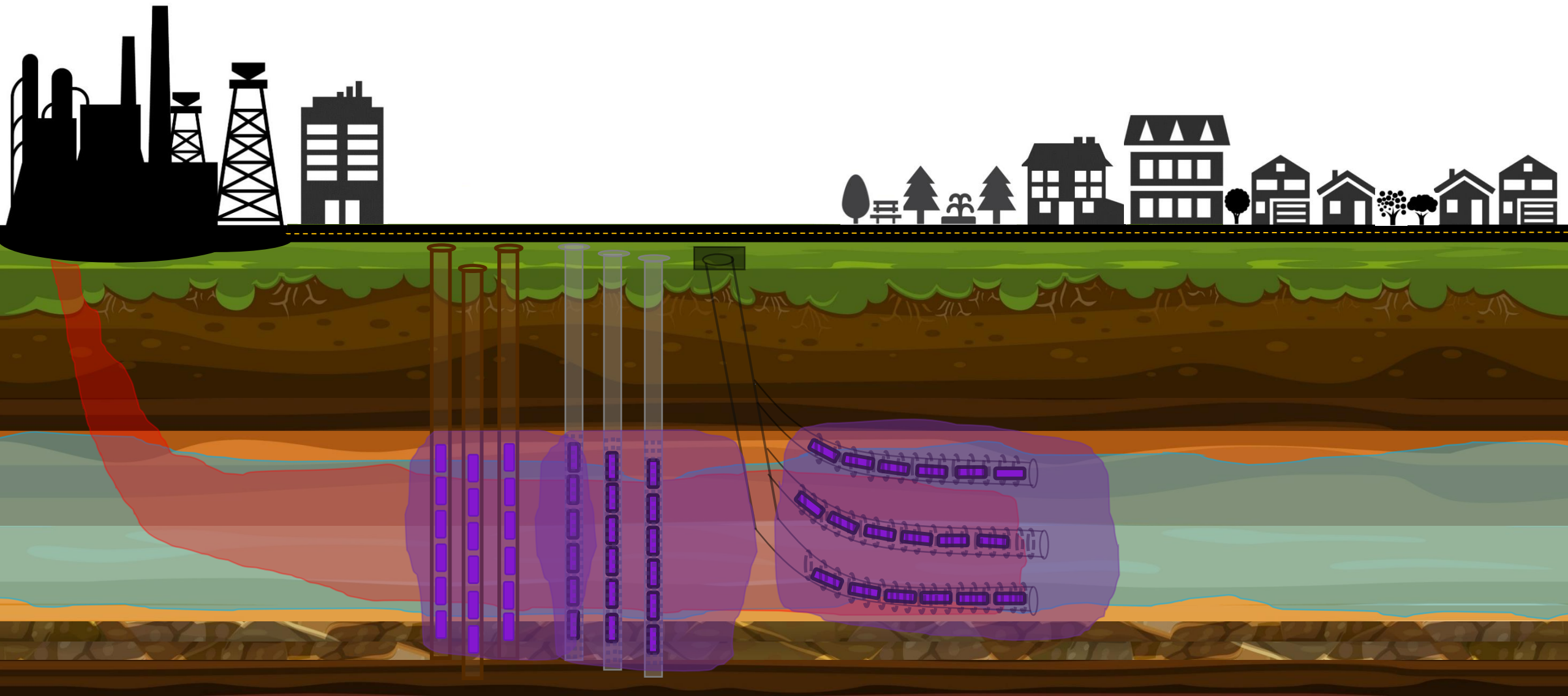
SOCORE – horizontal well/DD-PRB installation



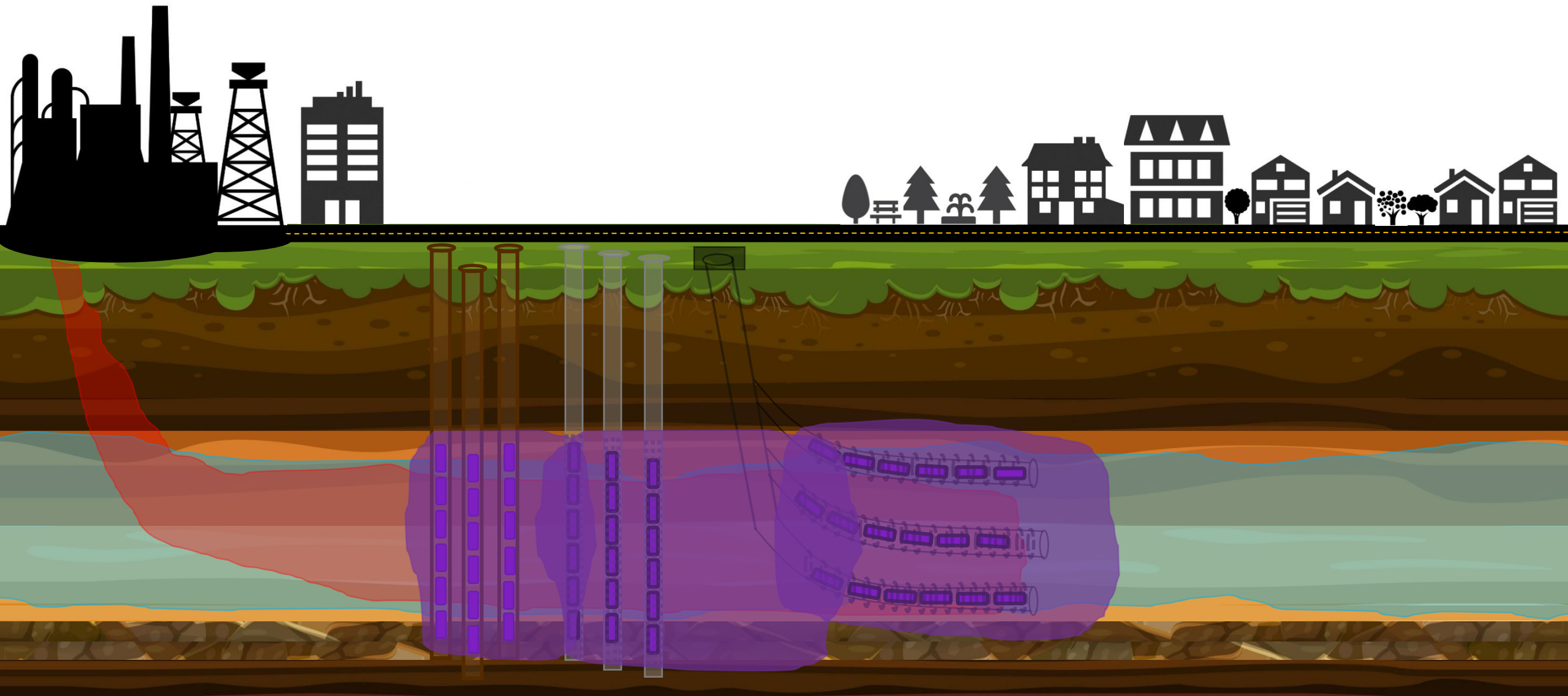
SOCORE – reactant release and distribution



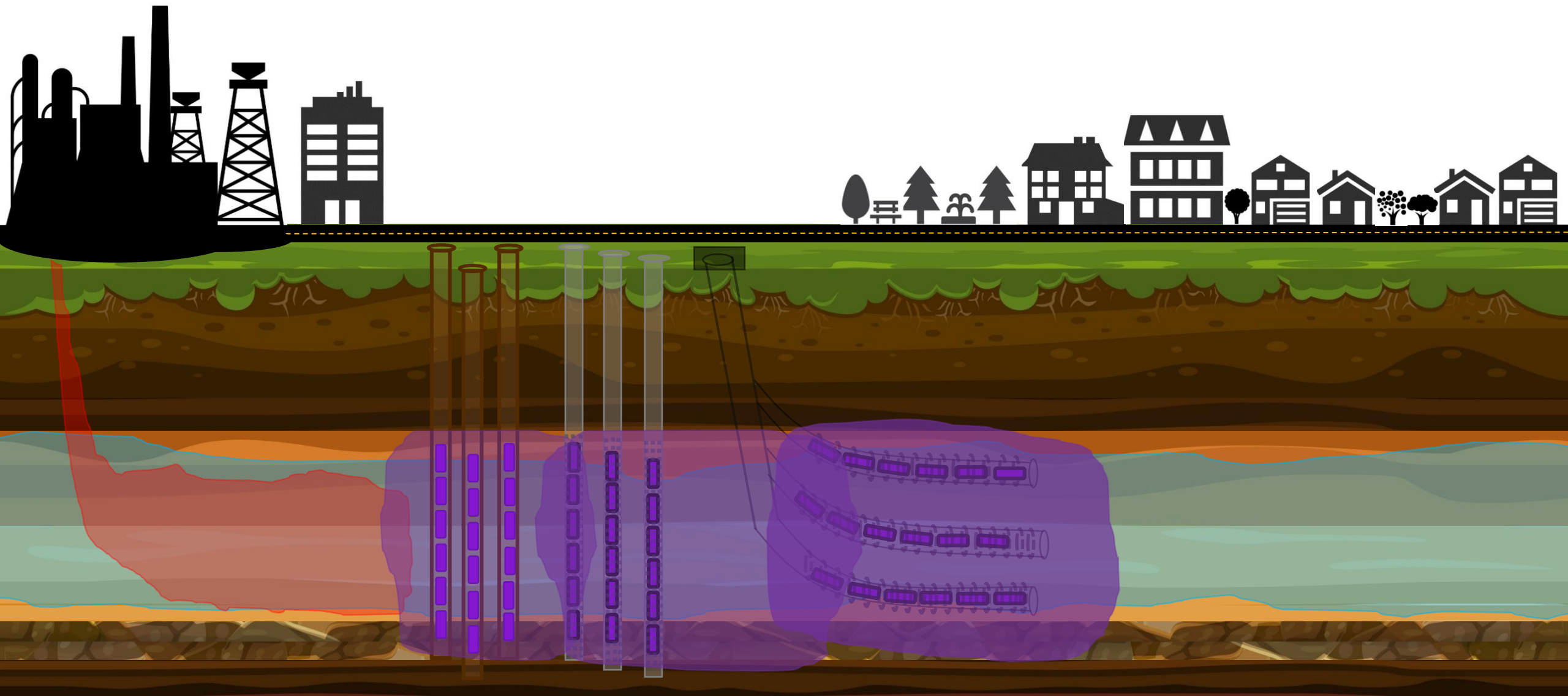
SOCORE – reactant release and distribution continued



SOCORE – reactant release and distribution
continued....



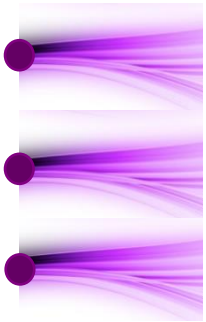
SOCORE – reactive zone established



Plume reduction/interception

Site Selection – When and where is SOCORE an appropriate remedial approach?

- Reactive Treatment/Interceptor Zones
- Saturated Conditions (**not** a vadose zone technology)
- Active facilities **or** remote locations where minimal remedial infrastructure is desired
- Heterogeneous formations and LPM where back diffusion would otherwise be problematic in a liquid application
- Remember stoichiometry – **don't under-dose the application**....there is no magical chemistry



CASE STUDY #1 (New Jersey)



Background:

Low-Cost, Low- Maintenance, and Green Reactive Treatment Zone

COC's - **PCE**, TCE, DCE, VC in GW
(100,000+ug/L total targeted CVOC in GW at source zone target well)

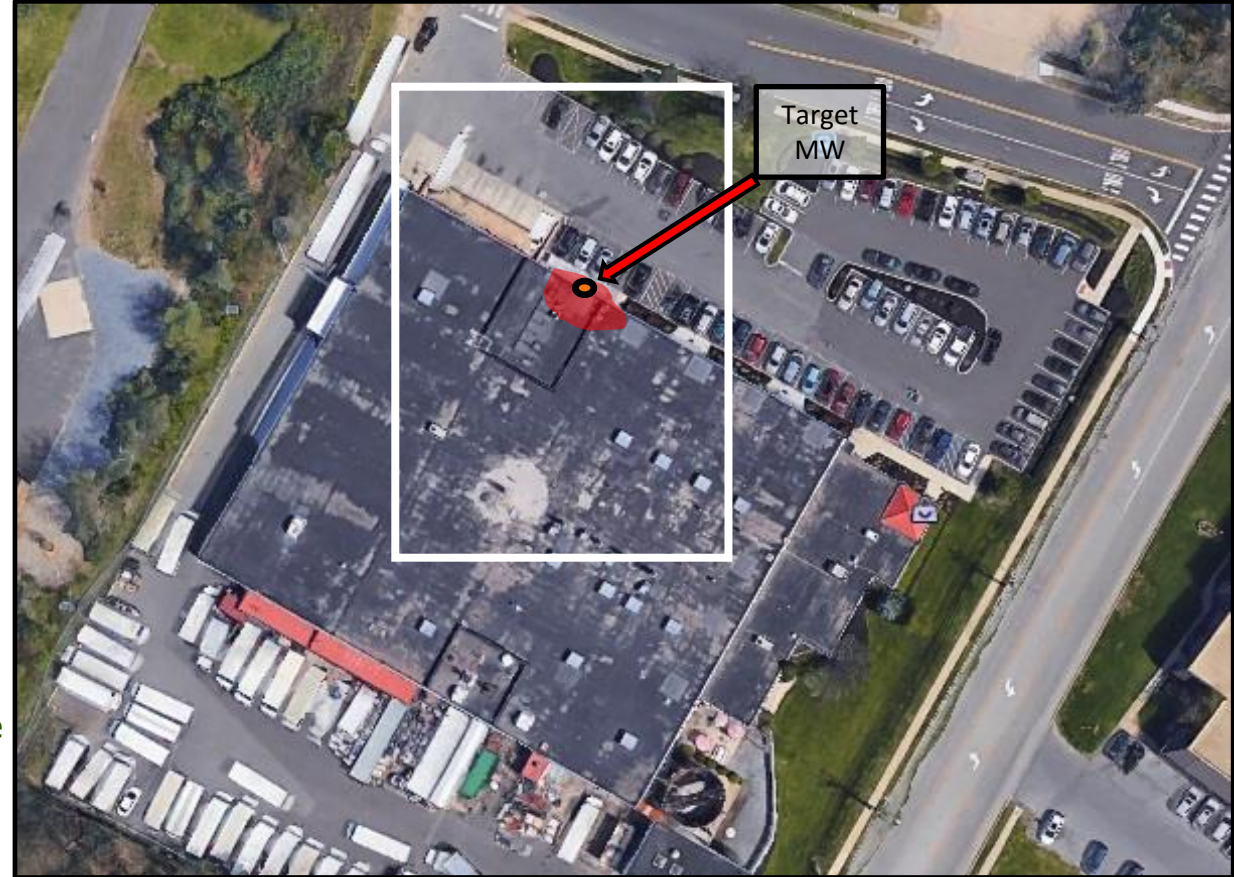
Geology - impacted fill to 10-12' bgs,
underlain by LPM clay formation

Site logistics:

- Active industrial facility
- Remaining source zone soils are located at **building foundation** and adjacent to **sewer utilities**
- Source remains in place

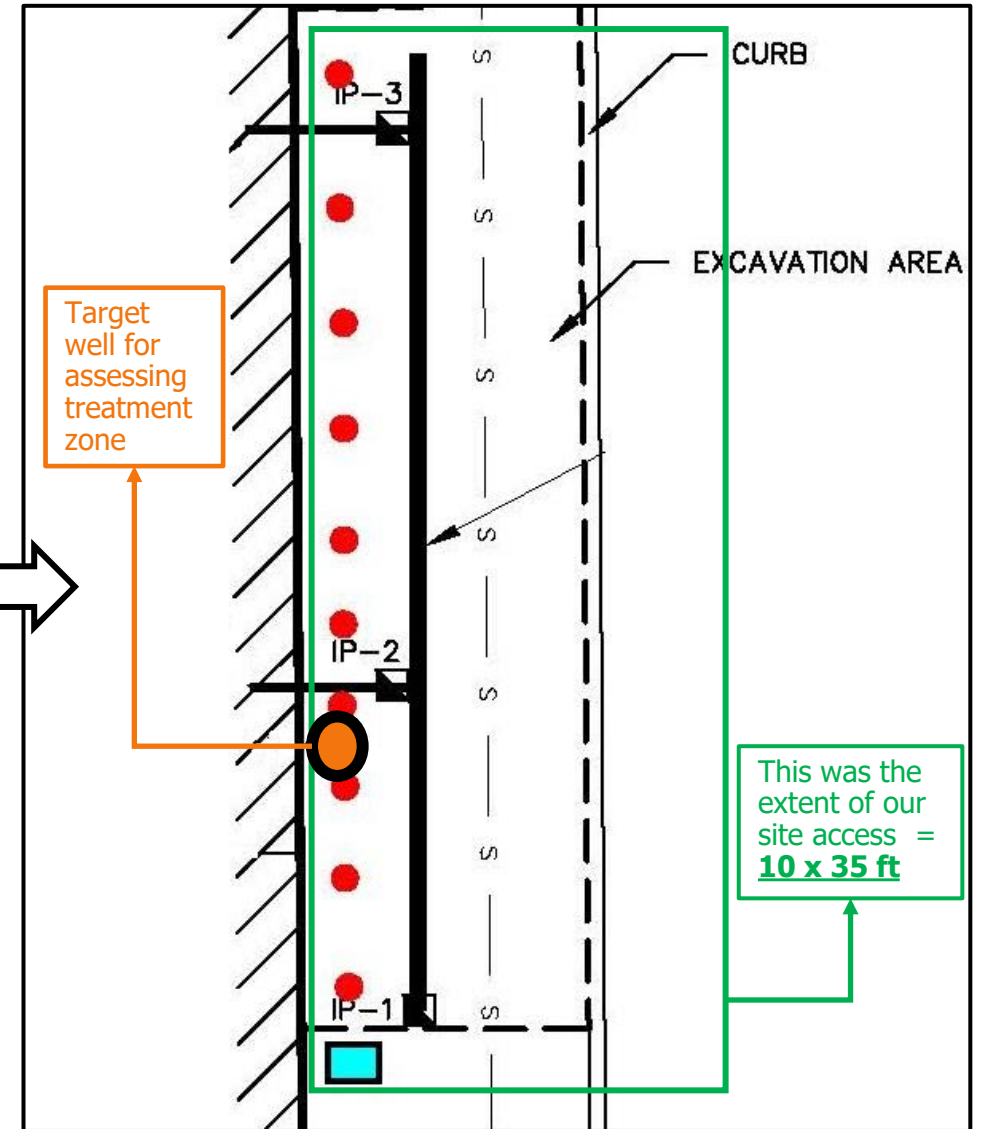
Previous remediation activities - extensive Free Product Recovery activities and limited source excavation, 2 RegenOx injections

Client's goals - seeking cost-effective and low-impact remedial strategy to address source area groundwater



Background:

Low-Cost, Low- Maintenance, and Green Reactive Treatment Zone



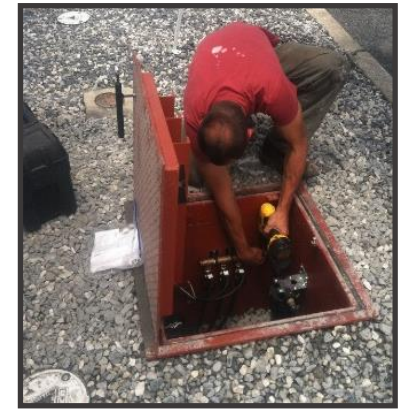
Remedial Approach:

3-Step Implementation



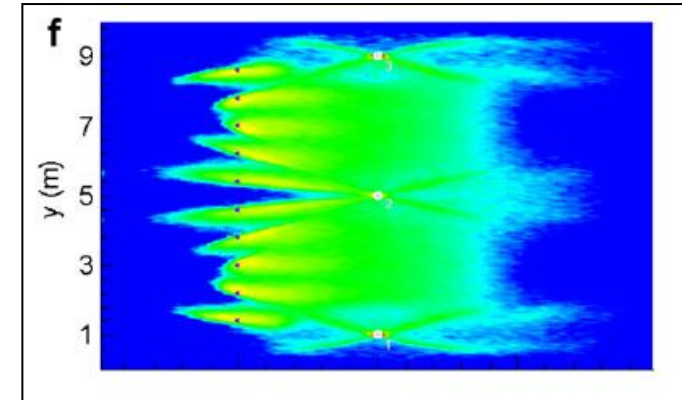
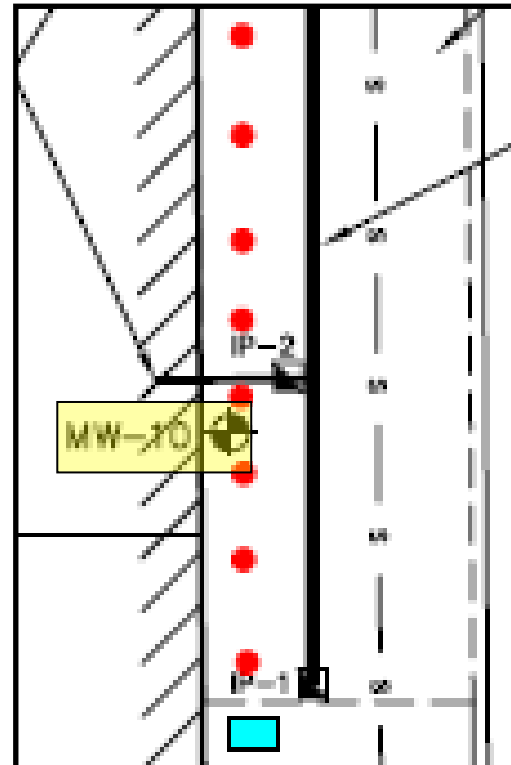
1) Injection

- 10 DPT boreholes
- Top down injection from 4'-10' bgs
- 40 gal of 10% NaMnO₄ per borehole from 4'-10' bgs
- followed by 25 gallon chase injections of clean water to assist distribution
- DPT boreholes placed on **3-foot spacings in a single row**



2) SOCORE –

- each borehole completed with 2" ID PVC piezometer screened from 2'-12" bgs (target interval)
- 4 SOCORE Permanganate cylinders with holders were deployed from 2' -12' bgs at each
- Total of 40 SOCORE Permanganate cylinders (1.35" x 24")



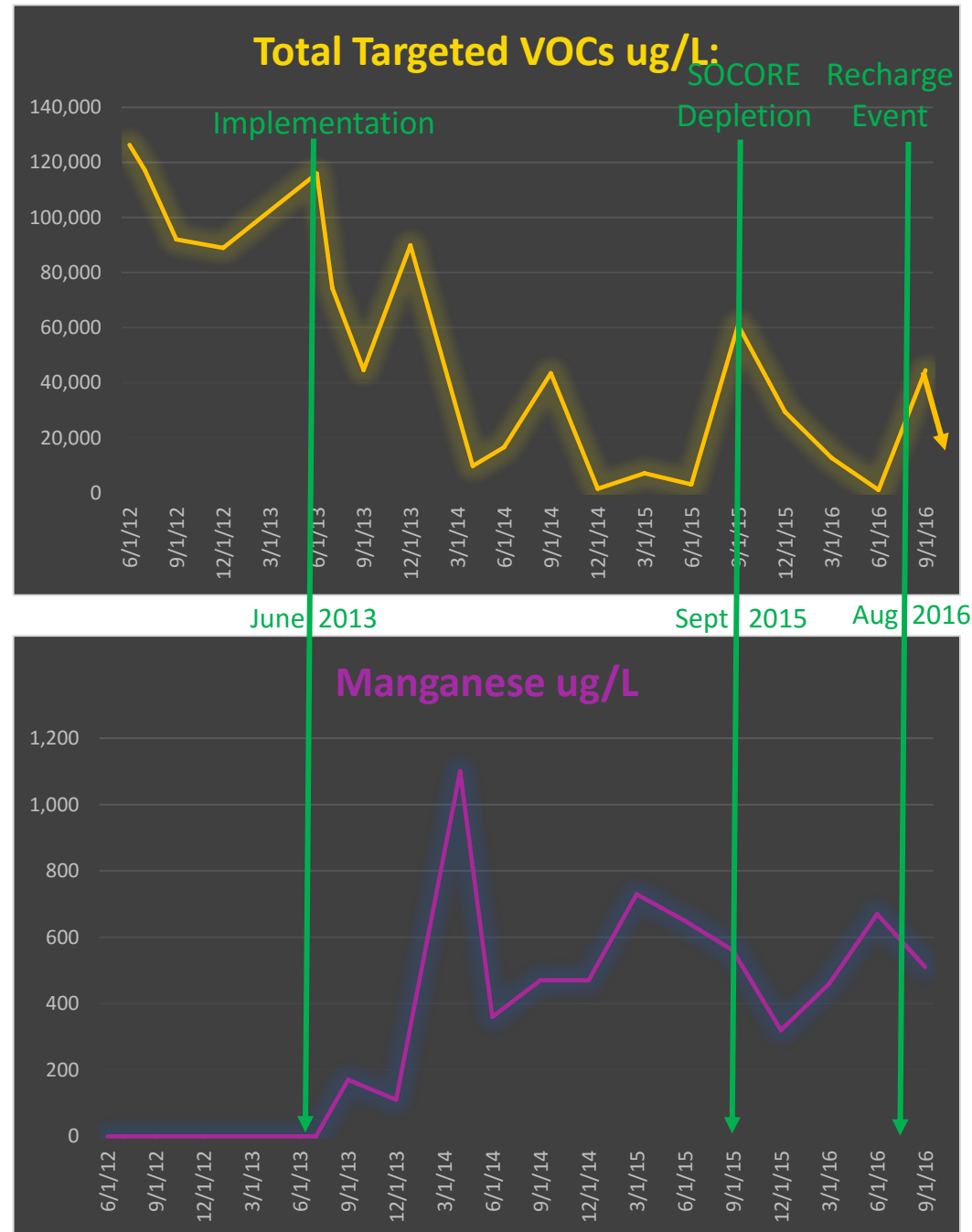
3) Recirculation –

- To accelerate KMnO₄ mixing/distribution across the reactive interceptor zone
- low-flow solar-powered recirculation system was also installed
- including: piston pump, manifolds, solenoid valves, programmable timer, and re-circulation lines.



Results:

Low-Cost, Low- Maintenance and, Green Reactive Interceptor Zone

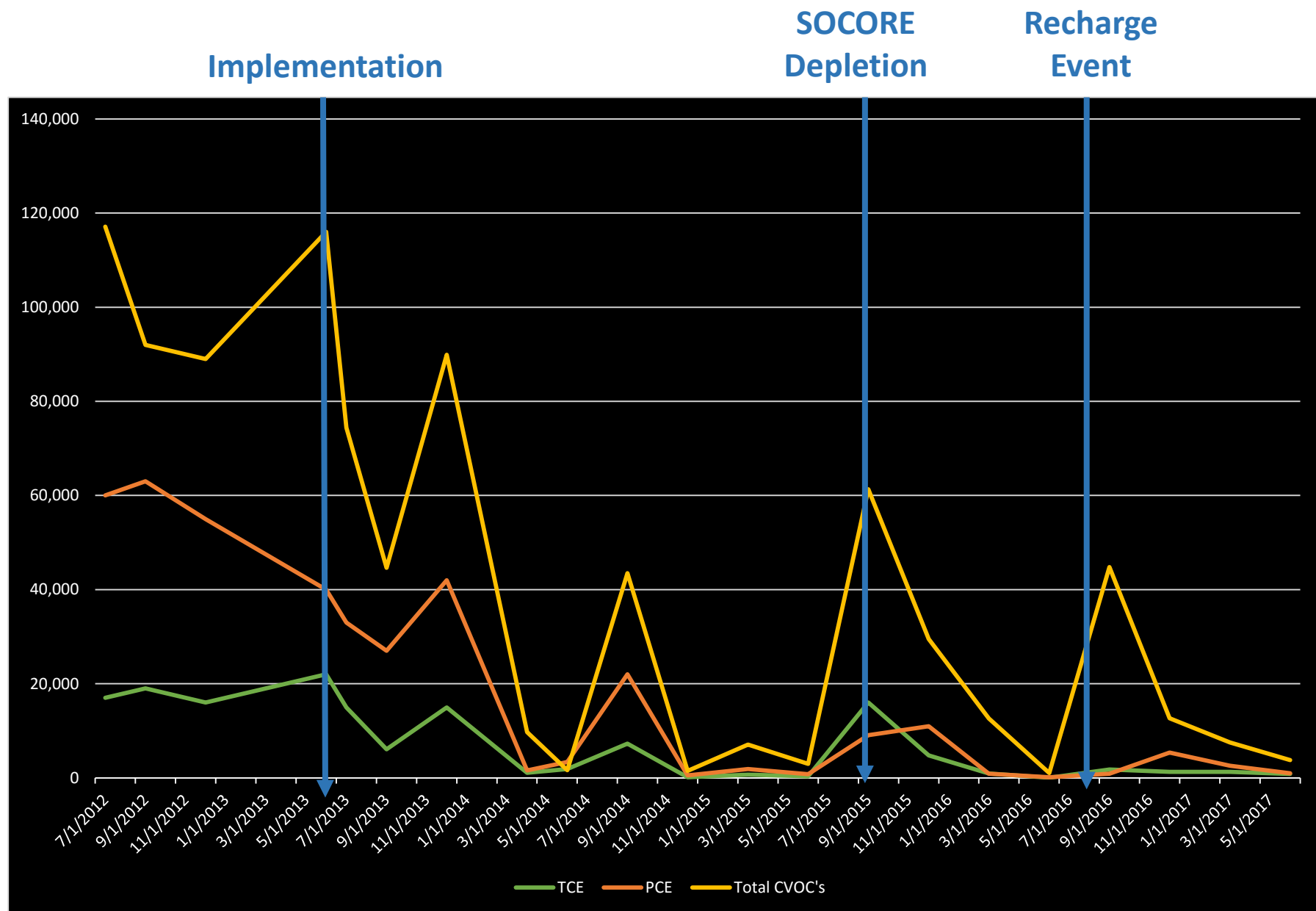


- The system was installed in June 2013 at a cost of **less than \$75,000.**
- VOC concentrations decreased at target monitoring well as expected
- 2.5 years after remedial implementation:
 - rising VOC concentrations
 - decreasing Mn concentrations
 - SOCORE Permanganate re-charge event was due
- The first SOCORE material **re-charge event was performed in August 2016 for less than \$10,000.**



Results:

Updated
GWM Data



CASE STUDY
#2
(Indiana)



Background:

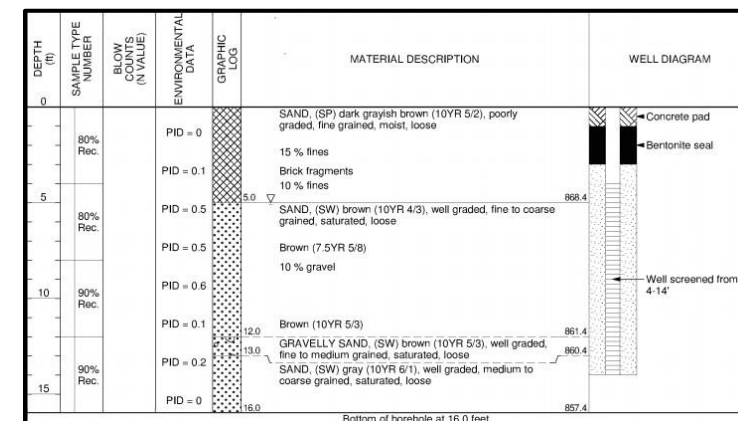
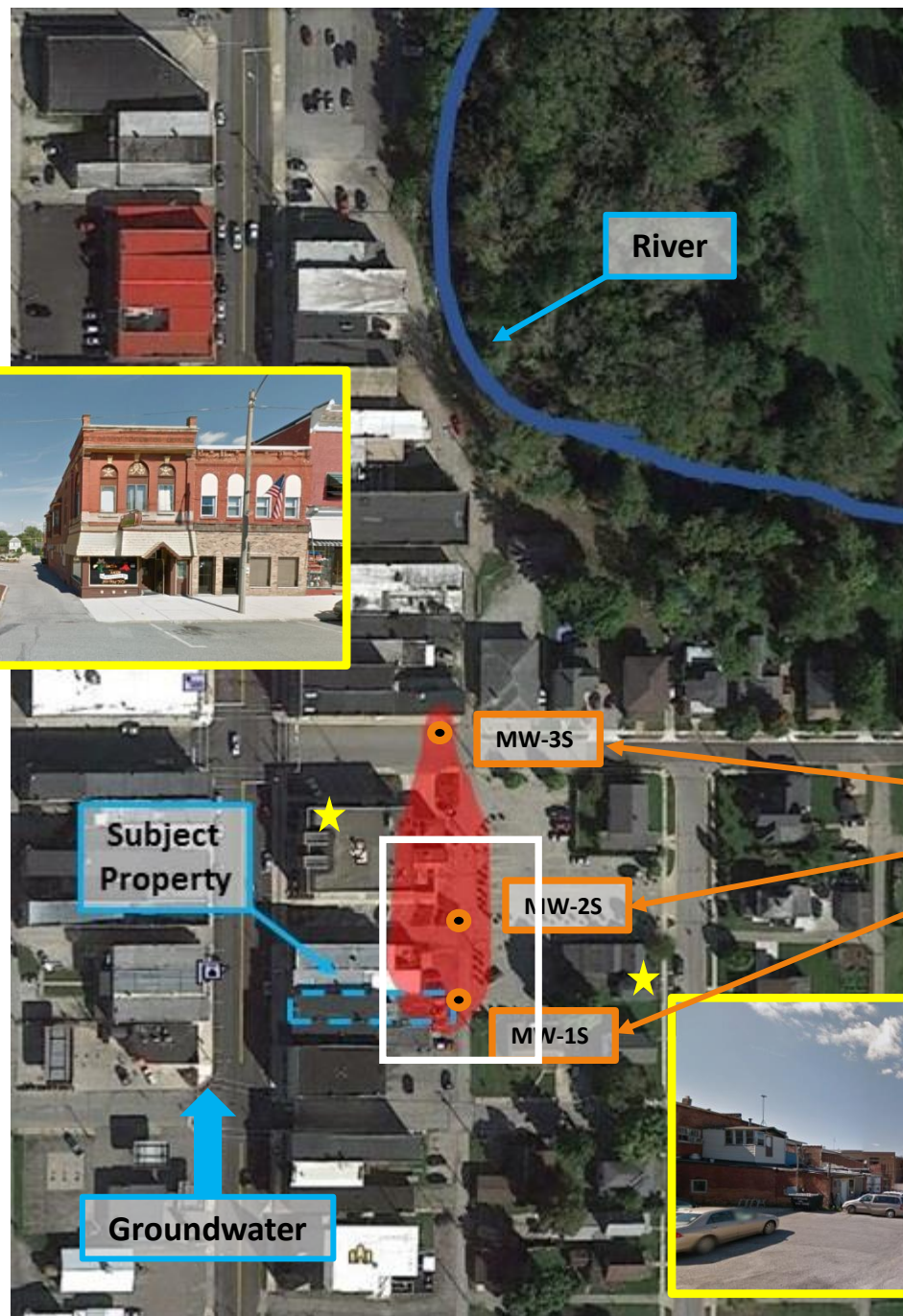
Reactive Treatment Zone & Interceptor Zone



- COC's - **PCE**, TCE, VC (**100-500 ug/L Total CVOC** concentration in GW)
- Geology - fill and sandy loam to 5' bgs, underlain by transmissive sands and gravelly sands
- Site logistics:
 - Remaining source zone soils are located behind building adjacent to **sewer utilities** and an alleyway
 - Neighboring properties include restaurants, retail store, City Hall and multiple **residences**
- Previous remediation activities – Shallow source zone soils excavation & **SVE/AS** mechanical remediation
- Client's goals – mitigate off-site migration of CVOC GW plume



Site Layout



Primarily Sands

	Screen	PCE	TCE	VC
MW-3S	6-16 ft	27.2	11	ND
MW-2S	5-15 ft	215	5.3	ND
MW-1S	6-16 ft	403	6.3	ND

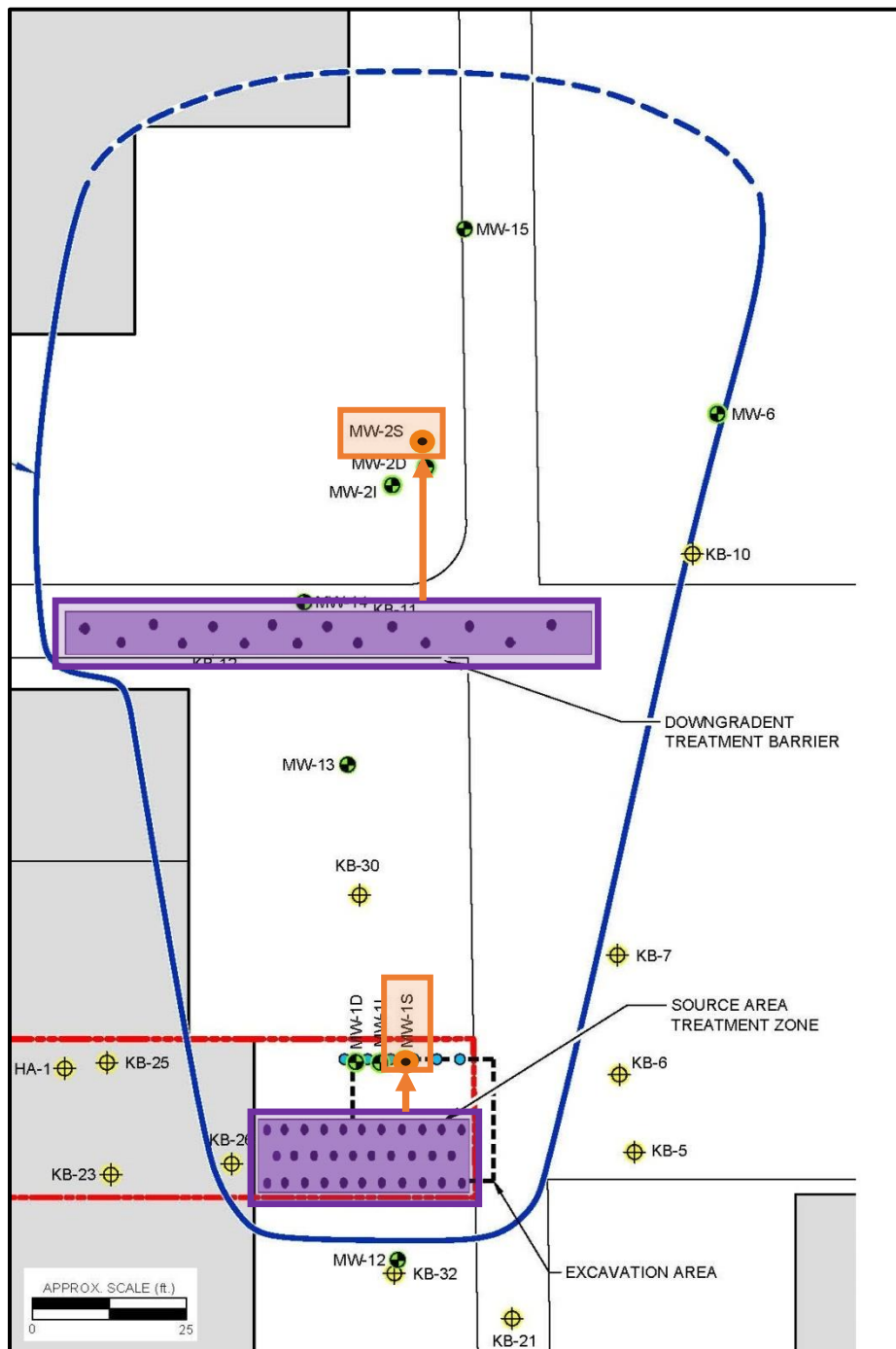


2 - Downgradient Treatment Interceptor:

- 90' wide x 10' deep - installation area
- (15) 3.25" DPT boreholes to 16' bgs
- 4 cylinders per borehole (8' – 16' bgs target interval)
- 2 rows, wider spacing than source area
- 60 SOCORE cylinders - 2.5" x 24" SOCORE Permanganate Cylinders
- Approx. 25 ft up-gradient from target well **MW-2S**

1 - Source Area Treatment Zone:

- 45' wide x 15' deep - installation area
- (35) 3.25" DPT boreholes to 16' bgs
- 3 cylinders per borehole (10' – 16' bgs target interval)
- 3 rows
- 105 SOCORE cylinders - 2.5" x 24" SOCORE Permanganate Cylinders
- Approx. 10 ft up-gradient from target well **MW-1S**



Site Layout:
SOCORE
Permanganate
Reactive
Zones

Site Photos



SOCORE Cylinders –
out of packaging



Preparing cylinders for
deployment down DPT
tooling



Geoprobe 6620 DPT - 50
boreholes to 16 fbg



Site Photos Continued



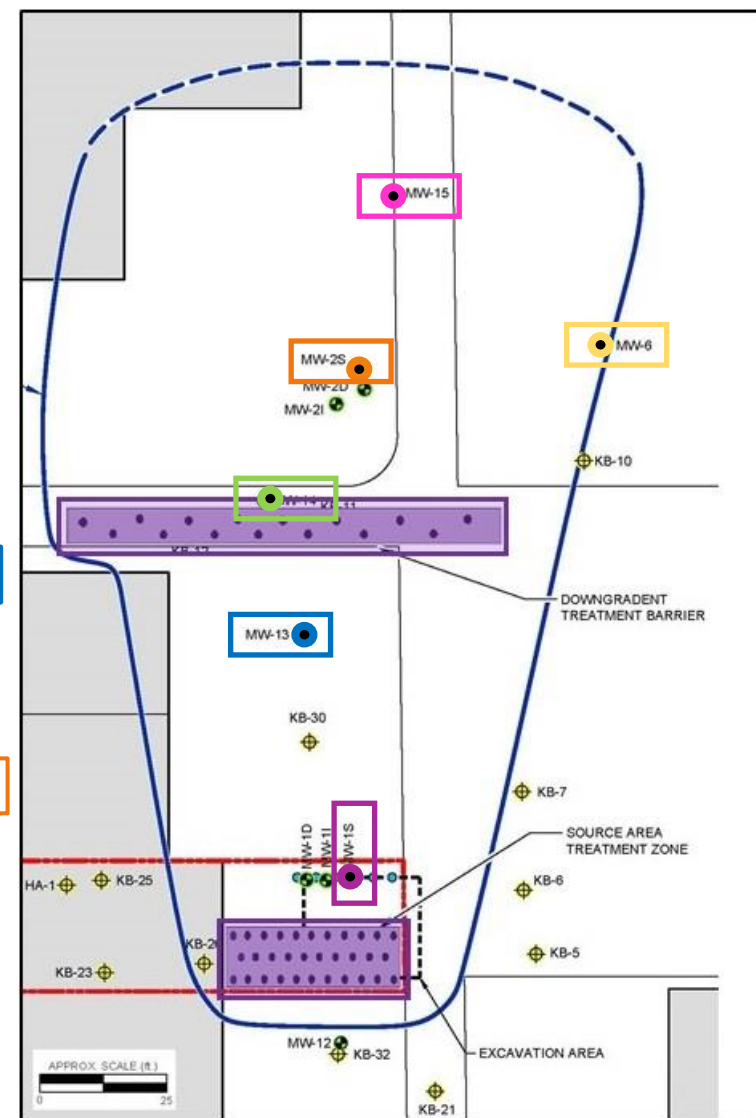
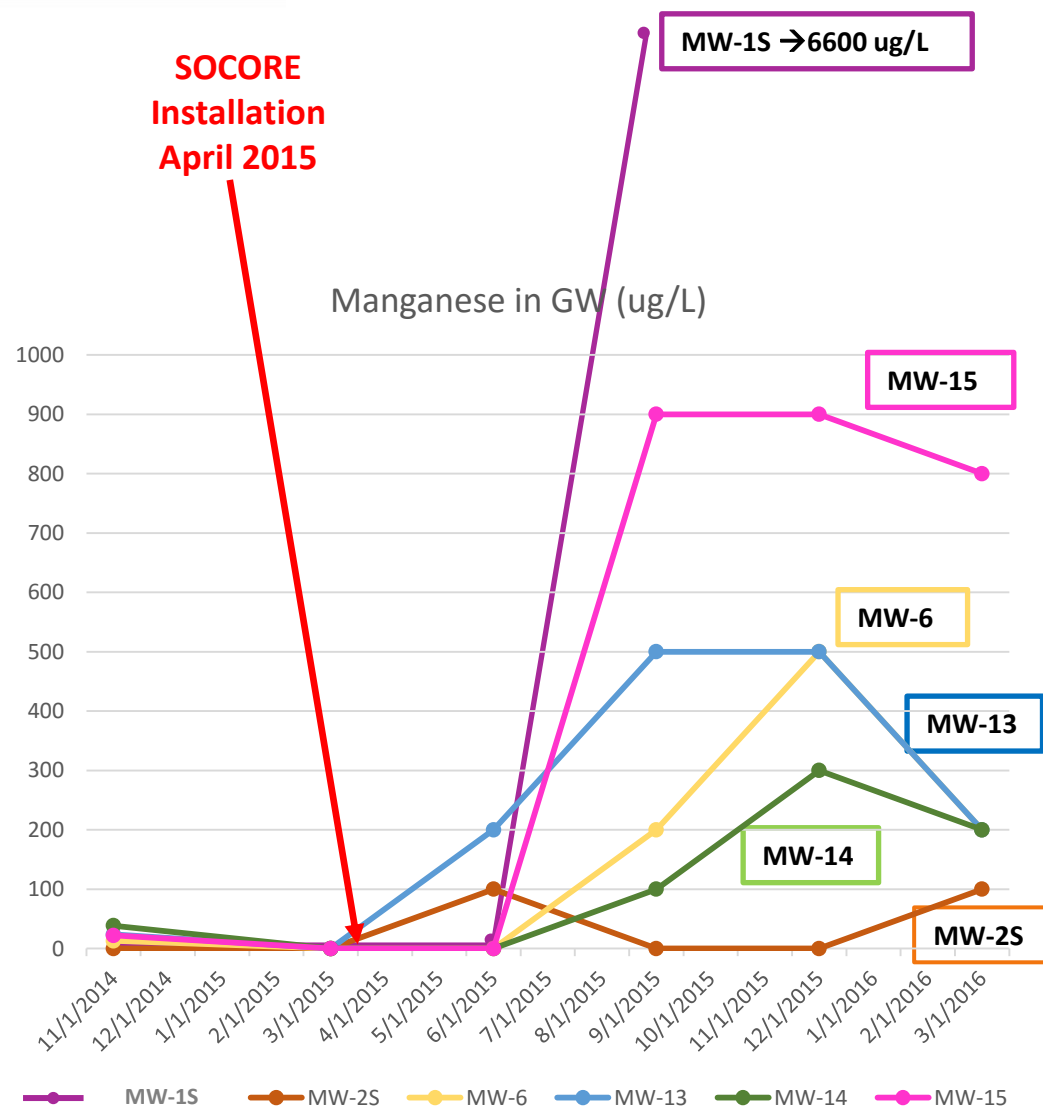
On-site SOCORE soil borings with nearby SVE manhole.



Downgradient SOCORE soil borings

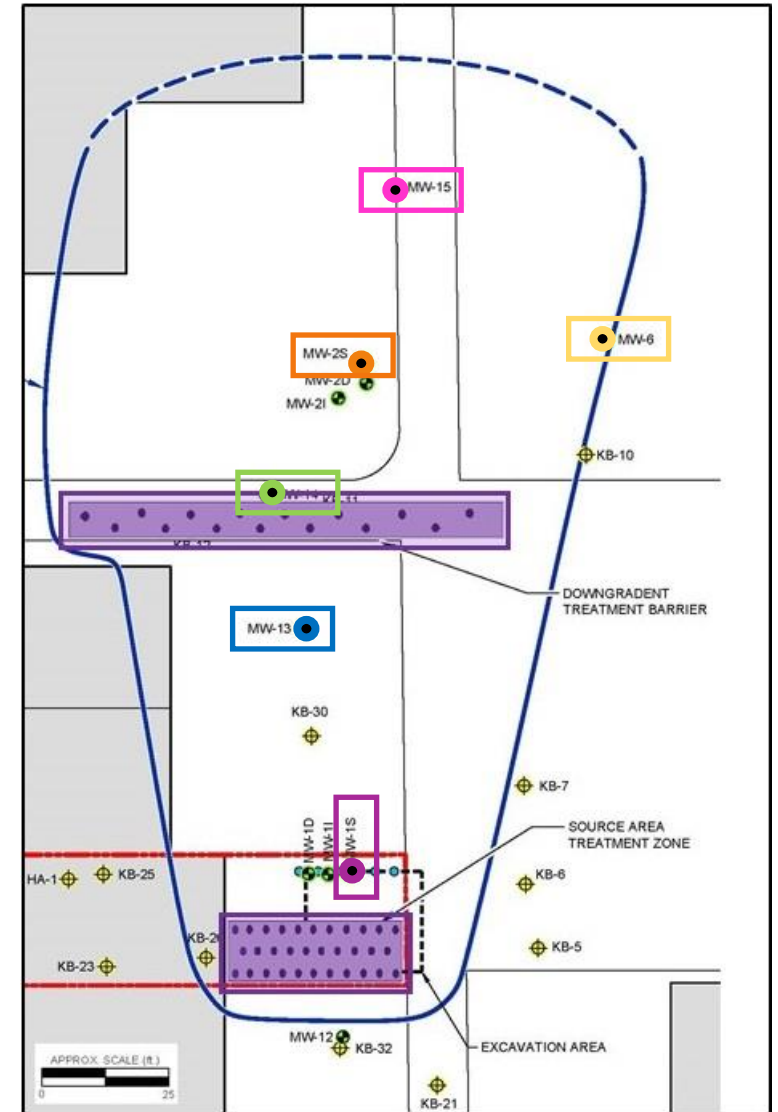
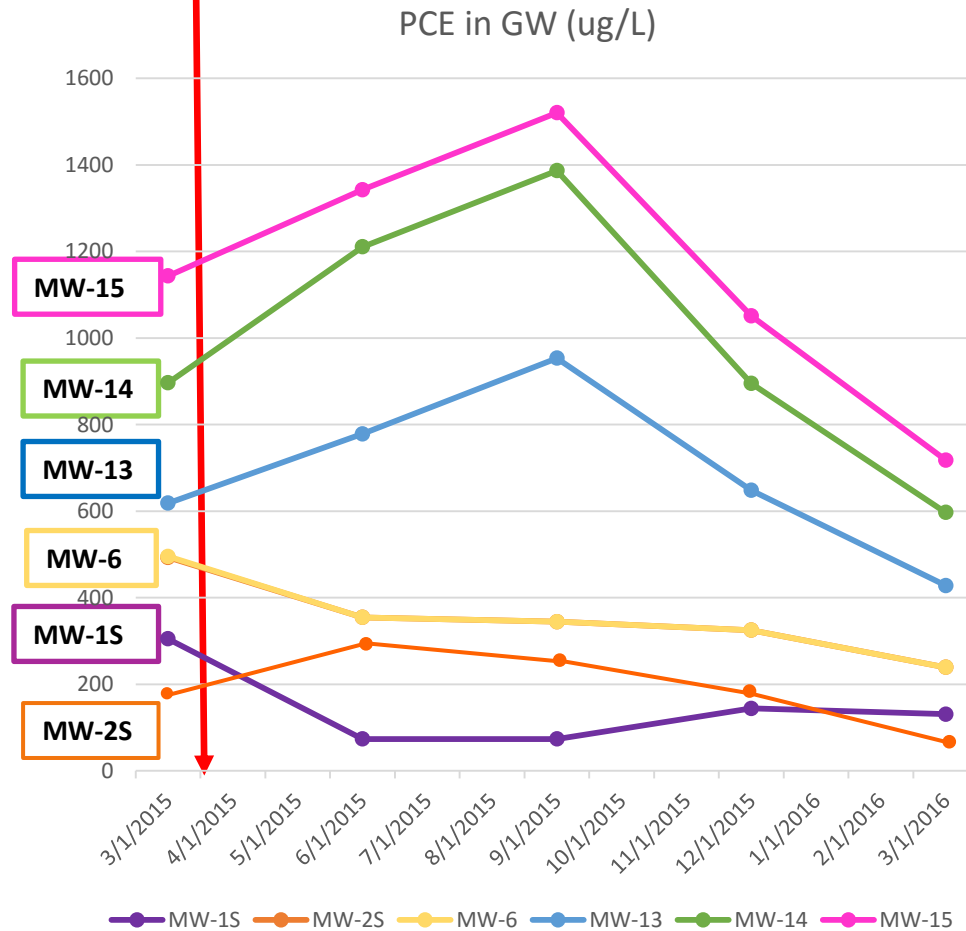


Results: MANGANESE



Results: PCE

**SOCORE
Installation
April 2015**



Cost and Time to Completion

TOTAL COST:

\$80,000

(materials & labor)

TIME TO COMPLETION:

4 days

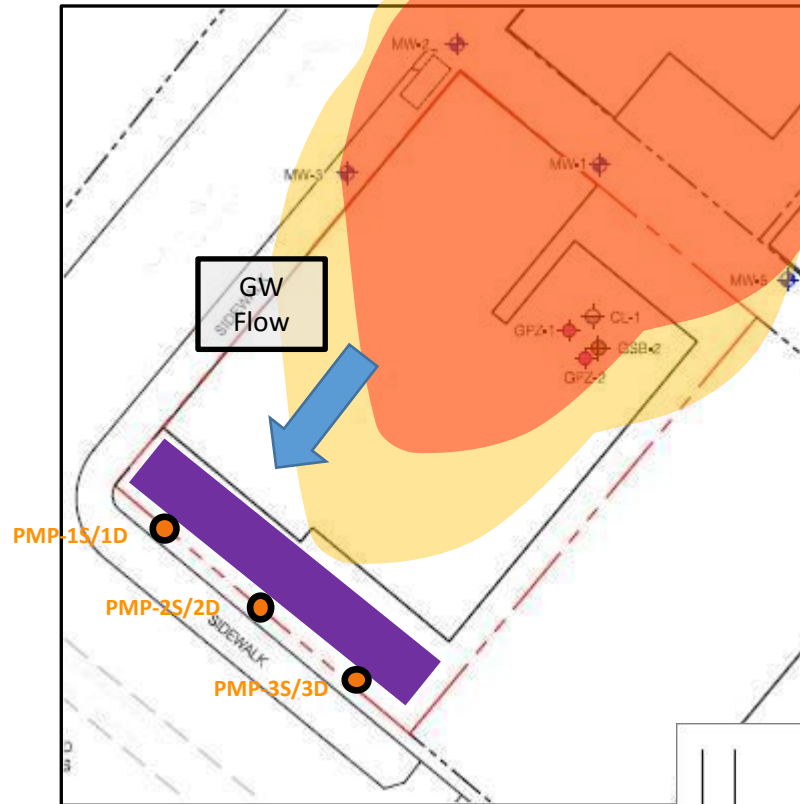



CASE STUDY
#3
(California)



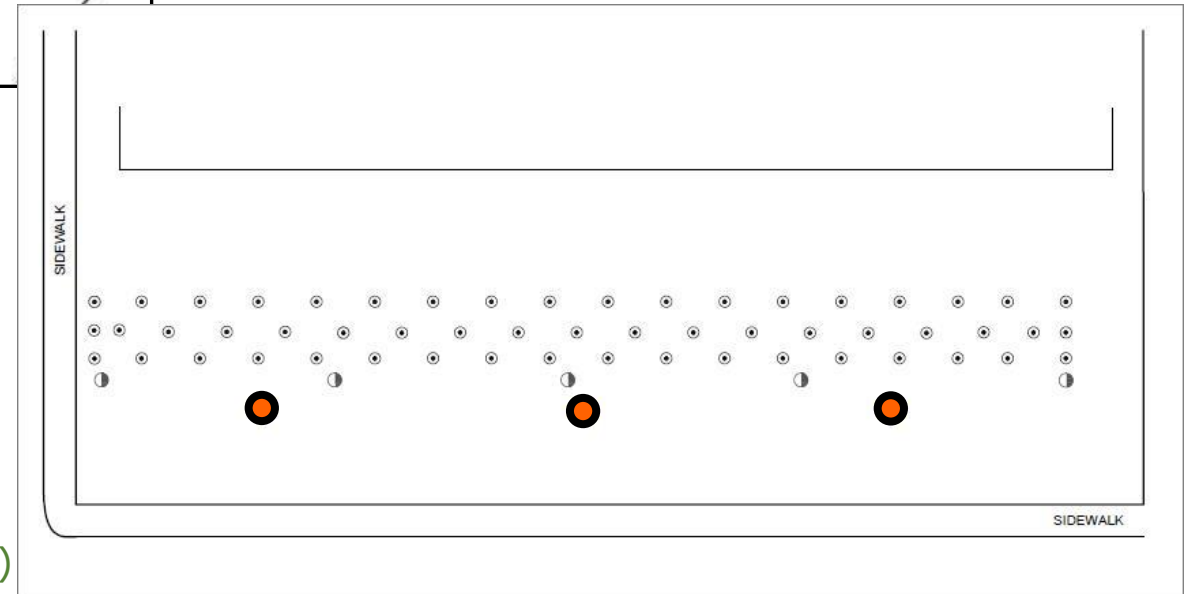
Background:

Reactive Interceptor Zone



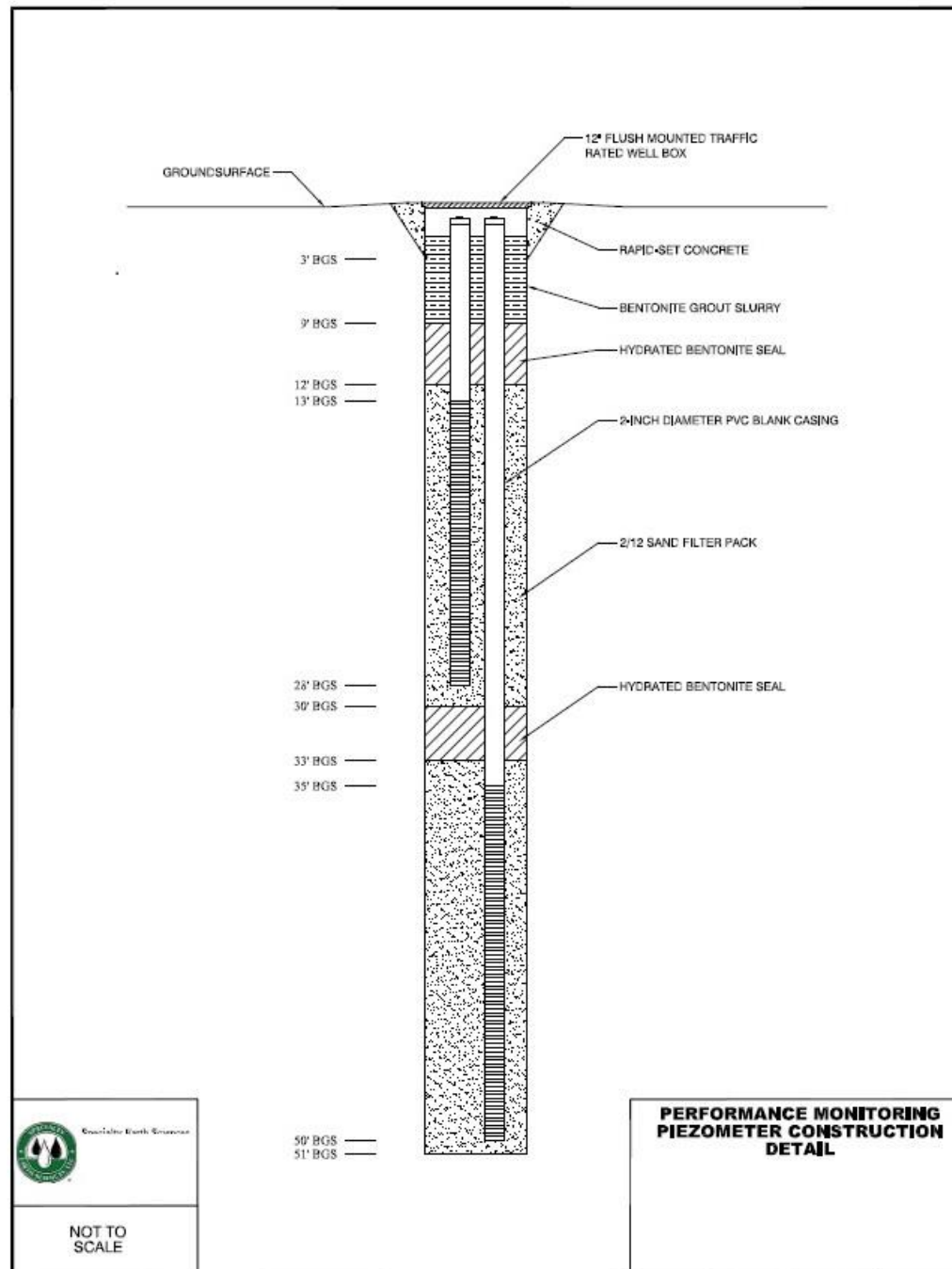
- Geology – stratified layers of bay muds and silty sands to 35' bgs, underlain by sands and silty sands
 - Impacted interval - 10'-40' bgs
- COC – CVOC's in GW migrating from up-gradient source (primarily PCE)
 - 10,000 ug/L baseline at PMP's ●
- Goal – mitigate further down-gradient plume migration 

- 51 boreholes –
 1. Top down permanganate injection
 2. completed with 2" piezometers for SOCORE deployment (459 total - 1.35" x 24" SOCORE Permanganate Cylinders)
- 3 (dual-nested) performance monitoring piezometers (PMP's) ●
- 5 permanganate obs piezometers (POP's)



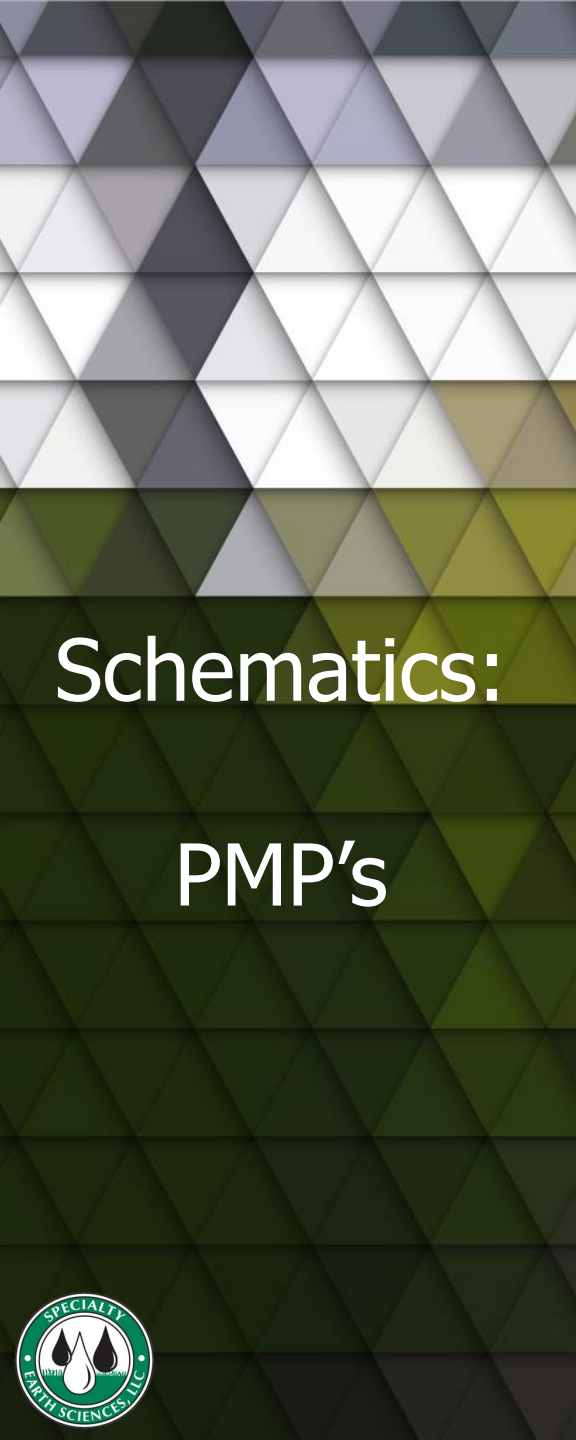
Schematics:

PMP's



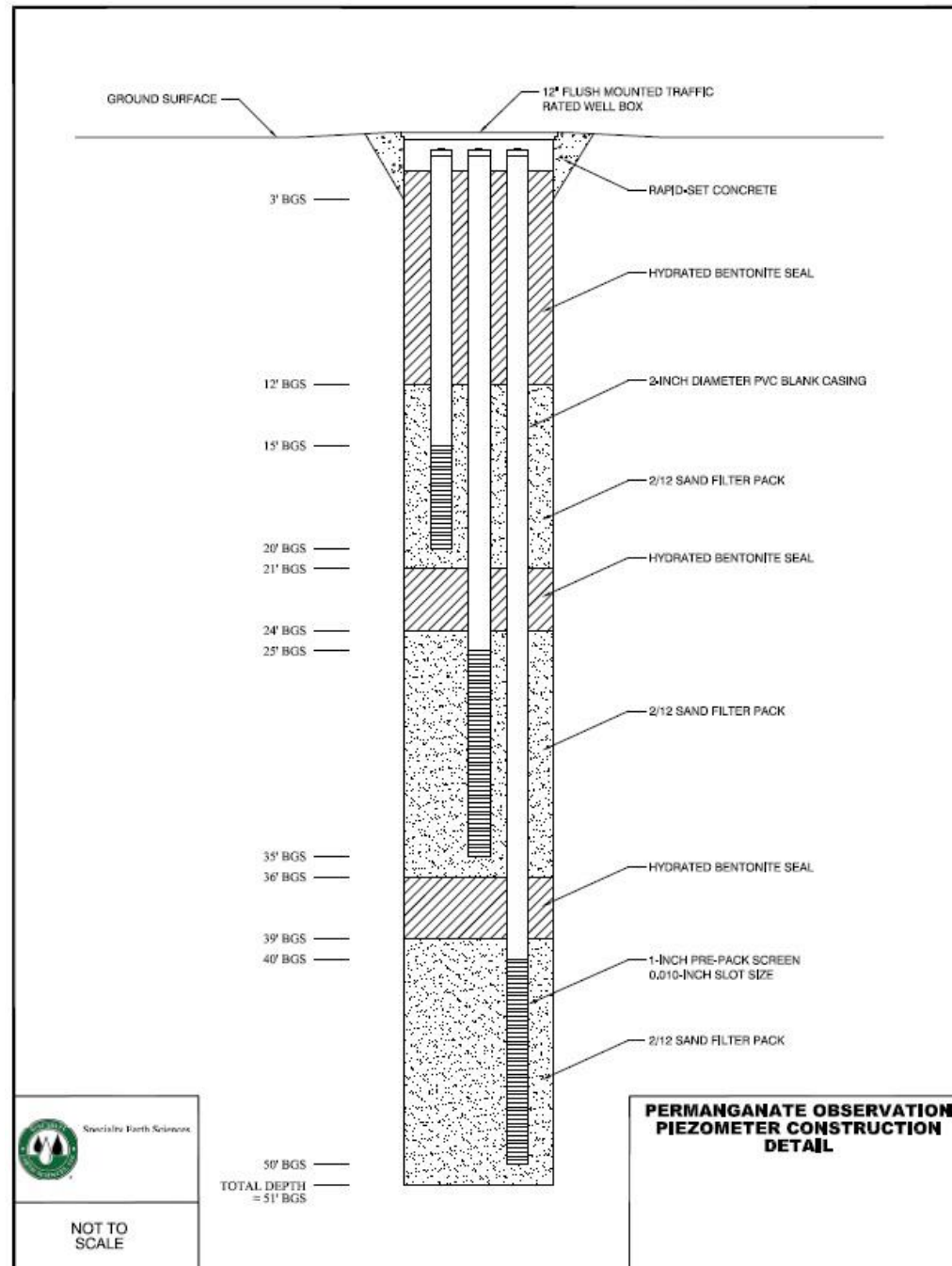
3 dual nested performance monitoring piezometers (PMP's):

- 15 feet of screen per piezometer
- Shallow & Deep Zones



Schematics:

POP's



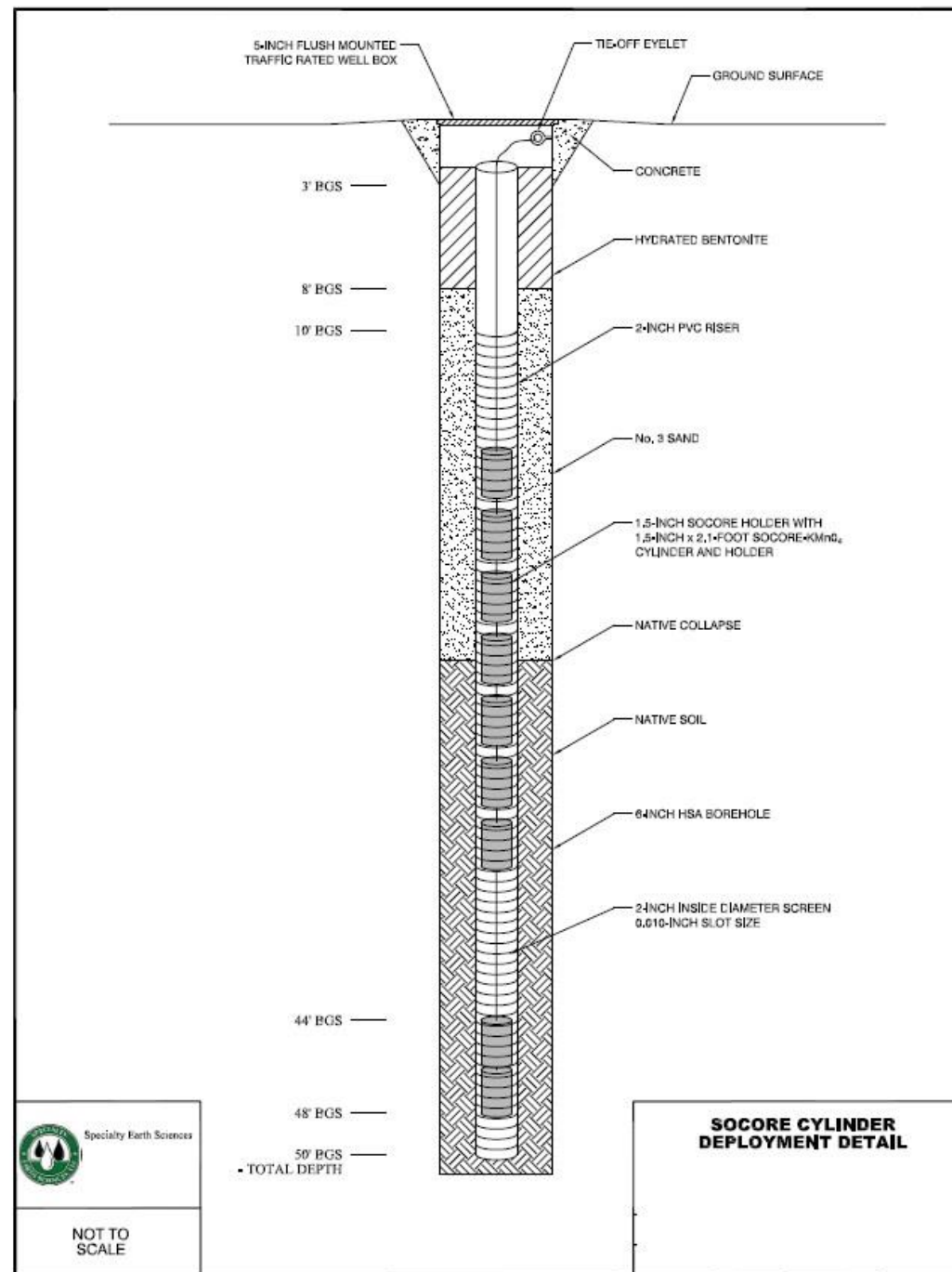
5 triple nested permanganate observation piezometers (POP's):

- 5-10 feet of screen per piezometer
- Shallow, Moderate, & Deep Zones



Schematics:

SOCORE deployment

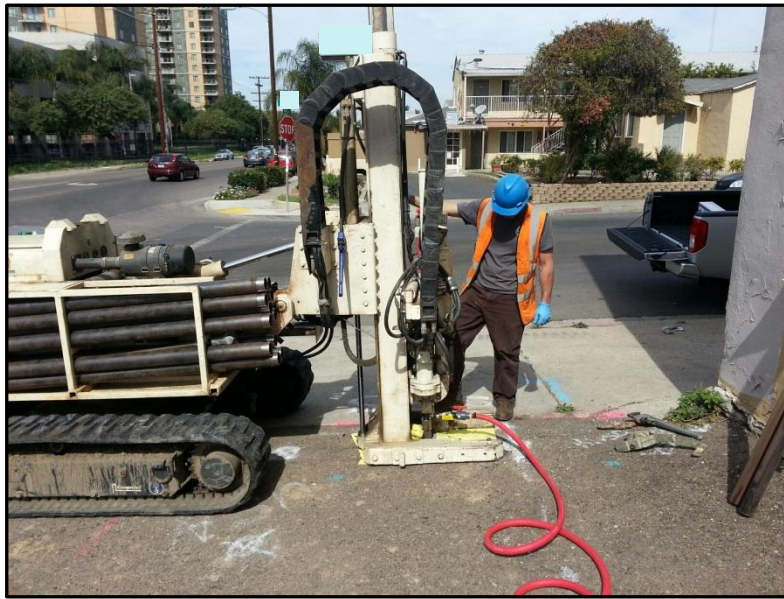


51 SOCORE deployment wells:

- 40 feet of screen per well
- 9 SOCORE holders and cylinders per well



Site Photos:

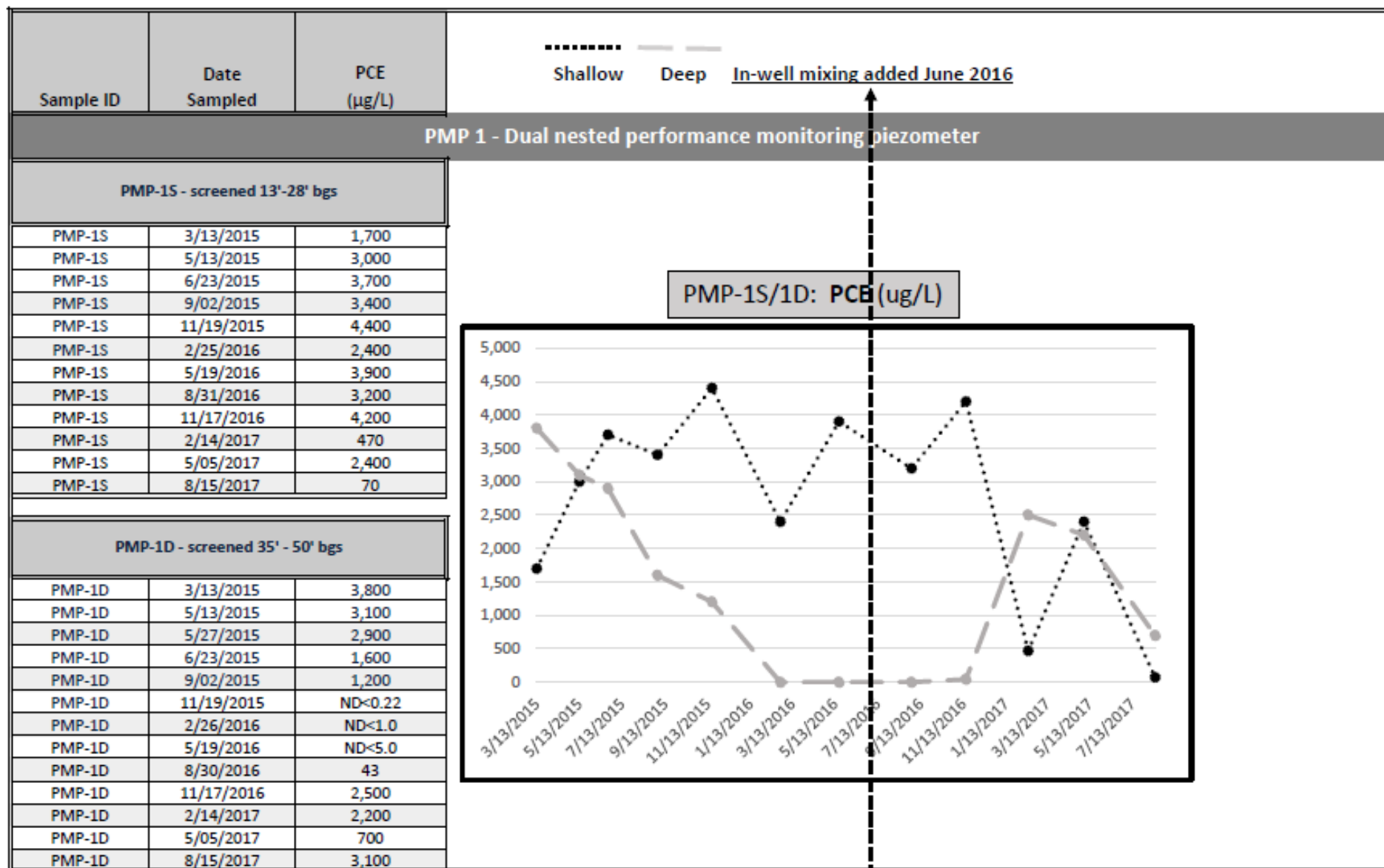


Site Photos:



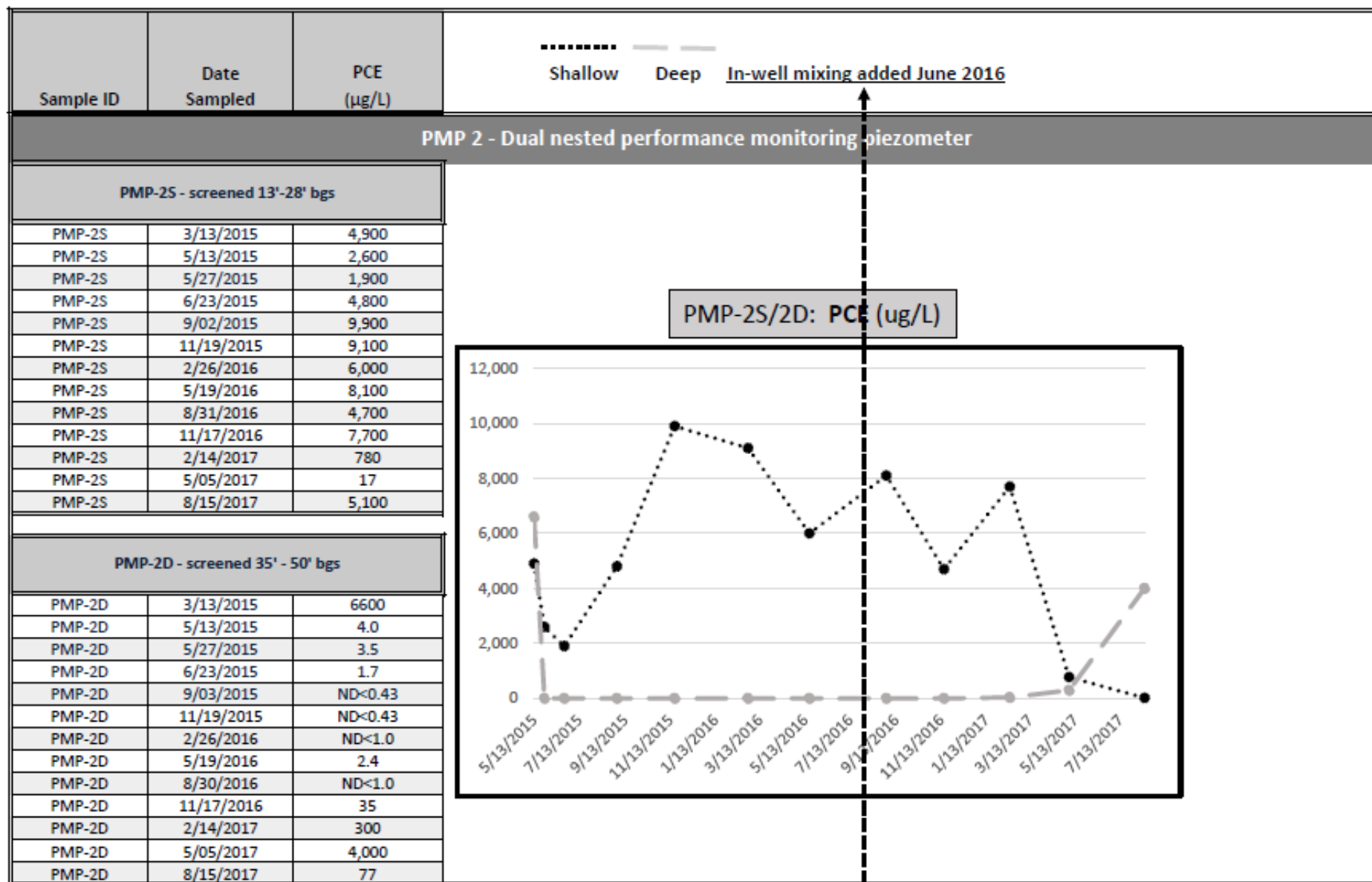
PCE Monitoring Data: PMP 1

PCE in Groundwater - PMP's



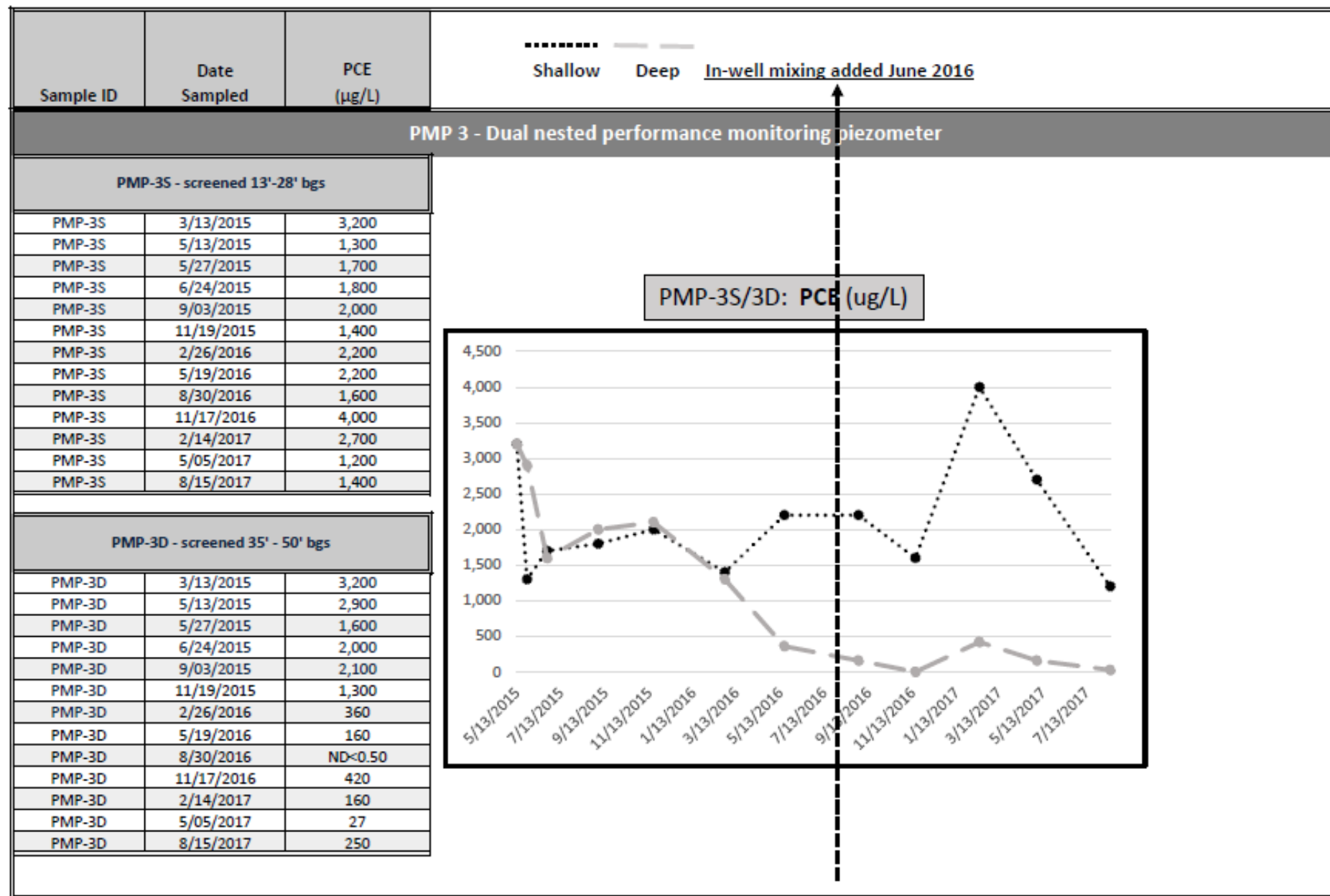
PCE Monitoring Data: PMP 2

PCE in Groundwater - PMP's

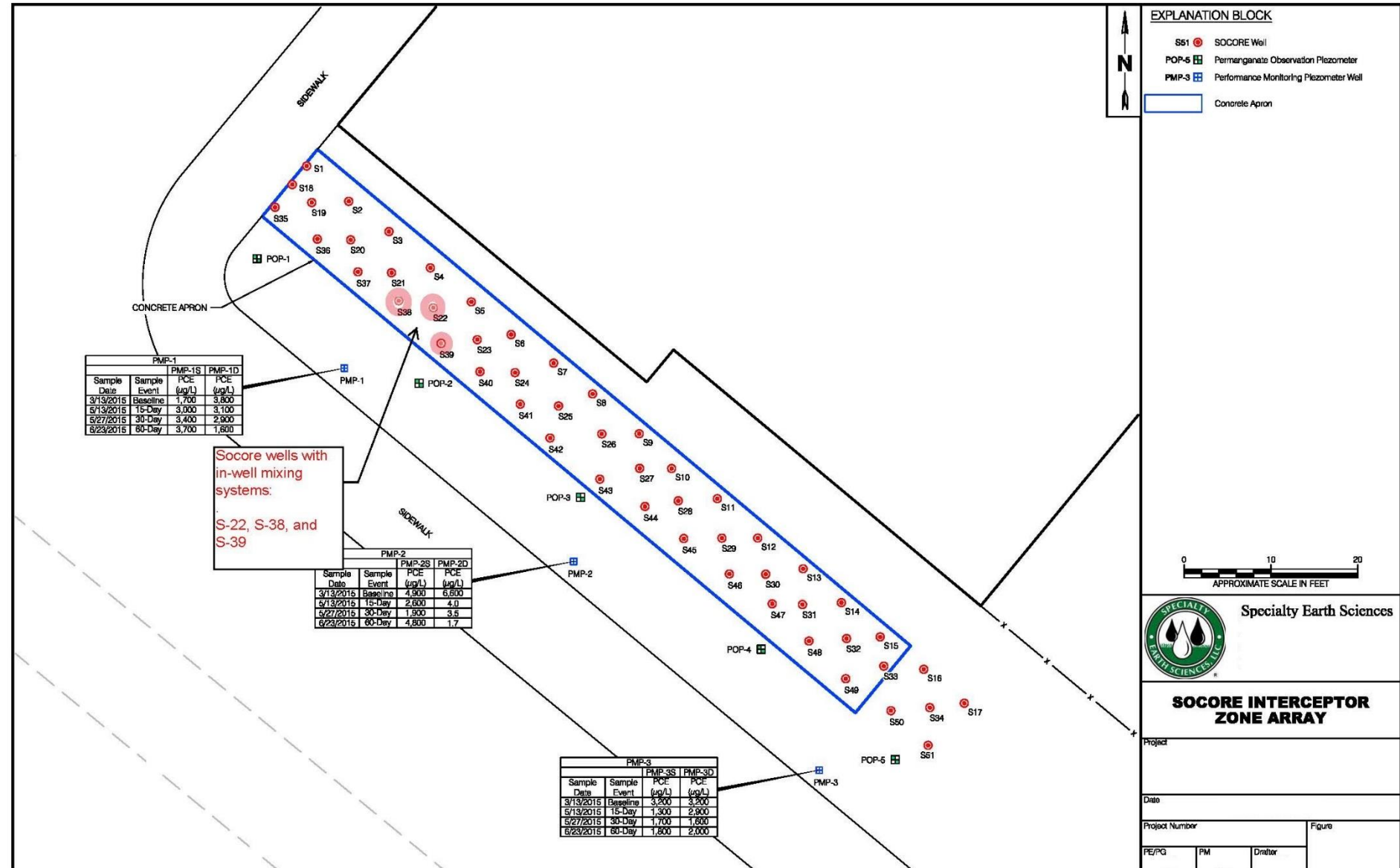


PCE Monitoring Data: PMP 3

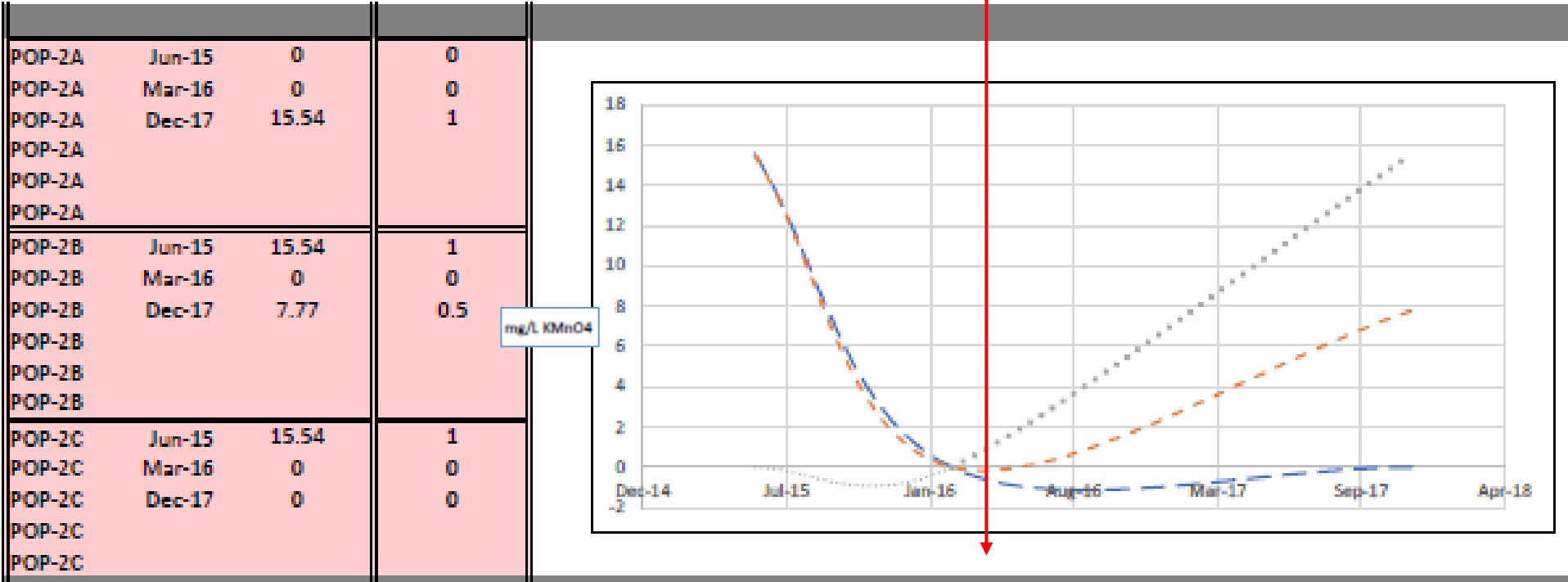
PCE in Groundwater - PMP's



In-well mixing



Permanganate Monitoring Data: POP-2



CASE STUDY
#4
(South Carolina)



CVOC Source Area Excavation, Soil Venting, Ex-Situ Oxidation...plus a little SOCORE



Baseline data:
9,000-11,000 mg/kg
PCE in source soils

2. Construct soil
venting mounds



3. Soil vapor
extraction and vapor
carbon treatment

SOCORE
Enhancement
to Alternate
Primary
Remediation
Techniques:

4. SOCORE
cylinders
across the
excavation
floor



5. Ex-situ permanganate
treatment of vented
source soils and backfill
into excavation

SOCORE
Enhancement
to Alternate
Primary
Remediation
Techniques:



RESULTS

- Completed remedial design, bench testing, full scale implementation and confirmation sampling for approx. \$430,000
- Alternate approach proposed by others (thermal desorption) was quoted at \$2,000,000

Background levels:
11,000 - 9,000 mg/kg

After Soil Venting:
1.3 – 0.18 mg/kg

After Chemical Application:
0.017 – 0.005 mg/kg

SOCORE
Enhancement
to Alternate
Primary
Remediation
Techniques:



Technical Pearls:

1. Safer and more efficient approach to ISCO
2. Targeted delivery of high concentration reactants
3. Reactive zones and interceptors
4. Addresses problems and challenges encountered with liquid injections
5. Cost to completion less than traditional ISCO injection
6. Implementation by on-site consultant



References:

Links to 3rd party publications can also be found on our website at:

www.sesciences.com
/technical-library



Specialty Earth Sciences IP:

US Patent No: 7,431,849
US Patent No: 8,210,773
US Patent No: 8,366,350
US Patent No: 9,061,333
US Patent No: 9,611,421
Japanese Patent No: 6,058,708
US Pat App No: 12-269,520
US Pat App No: 13-088,217
US Pat App No: 13-731,735
US Pat App No: 14-024,046
US Pat App No: 14-920,370
EU Pat App No: 09 826 642.2-1371

Related Publications:

Christenson et al, The Water Center, 2016
Kambhu et al, *Chemosphere*, 2012, 89, 656-664.
Christenson et al, *Chemosphere*, 2012, 89, 680-687.
Woo et al, *Env Tech*, 2009, 30, 1337-1342
Luster-Teasley, *Proceedings of 2007 Natnl Conf on Env Sci and Tech*.
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Lee et al, *Chemosphere*, 2007, 71, 902-910
Lee and Schwartz, *Chemosphere*, 2007, 69, 247-253.
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Ross et al *Journal of Environ. Eng.*, 2005, Vol. 131, 1203-1210.
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- Yang 2016 – “To postpone the precipitation of manganese oxides in the degradation of tetrachloroethylene by controlling the permanganate concentration”
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